Integrated Master in Chemical Engineering

MEAs preparation via wet routes for PEM electrolysis

Master Thesis

By

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Abstract

Hydrogen can be the optimal energy carrier to store the surplus of renewable and intermittent power sources. PEM (Proton Exchange Membrane) electrolysis provides a sustainable solution for the production of hydrogen. A new MEA (Membrane Electrode Assembly) was developed for PEM electrolyzers via wet coating routes, such as screen printing technique. Cost reduction in the production of MEAs is one the main requirements for effective and economical attractiveness of this technology.

Thin and reproducible catalyst layers were developed, mainly addressing the anode side particularities due to the slow kinetics of the oxygen evolution reaction. Electrochemical tests were performed using a fast and simple electrolyzer assembly. Some assembly features were studied in order to standardize optimum assembly reproducibility. Different organic solvents were used in catalyst inks and their electrochemical performance influence was studied. In order to overcome swelling caused by some of those organic solvents, a swelling treatment to the membrane was proposed and its electrochemical activity effects were characterized. Developed MEAs were electrochemically compared with commercial MEAs.

Developed anode electrodes were directly deposited on the membrane by screen printing technique. After establishing a highly reproducible cell assembly, cyclohexanol proved to be the most suitable single solvent for producing MEA electrodes by screen printing technique. When compared with a commercial MEA from Solvicore®, developed MEAs showed 30 % of electrochemical activity with five times less anode catalyst loading (0.4 mg cm^{-2} of Iridium). Performance characterization, of the developed MEAs, should be completed with longer polarizations in order to collect enough data for electrochemical durability considerations. The proposed swelling treatment proved to be effective, contributing for better coating reproducibility when using organic solvents that promote membrane swelling.

Keywords: PEM water electrolysis, membrane electrodes assembly, screen printing technique, membrane swelling.

Resumo

A produção electroquímica de hidrogénio pode ser a abordagem ótima para armazenar o excedente proveniente de fontes energéticas renováveis e intermitentes. Eletrólise, do tipo *PEM (Proton Exchange Membrane)*, providencia uma solução sustentável para a produção de hidrogénio de elevada pureza. Foi desenvolvida uma nova *MEA (Membrane Electrode Assembly)* para eletrolisadores através do método de impressão à tela. Reduzir custos de produção de *MEAs* é um dos principais requisitos para atrair industrialização desta tecnologia.

Foram desenvolvidos eletrodos finos e reprodutíveis, principalmente direcionados às particularidades do ânodo, devido à lenta cinética da reação. Montou-se um eletrolisador simples para testes eletroquímicos às *MEAs* desenvolvidas e estudou-se algumas particularidades da montagem, de modo a otimizar a mesma. Foram utilizados vários solventes orgânicos nas pastas catalíticas e a sua influência no desempenho eletroquímico foi estudada. De forma a ultrapassar o inchamento causado por alguns dos solventes orgânicos, foi proposto um tratamento de inchamento à membrana e foram caracterizados os seus efeitos na atividade eletroquímica. As *MEAs* desenvolvidas foram comparadas eletroquimicamente com *MEAs* comerciais.

Os ânodos desenvolvidos foram depositados diretamente na membrana. O solvente mais adequado para produzir elétrodos pelo método de impressão à tela foi o ciclohexanol. Quando comparado com uma *MEA* comercial apresentou 30 % da atividade eletroquímica com cinco vezes menos carga catalítica no ânodo (0.4 mg cm^{-2} de Irídio). A caracterização do desempenho das *MEAs* desenvolvidas deveria ser completada com polarizações mais longas para aferir a durabilidade eletroquímica das mesmas. O tratamento de inchamento da membrana que foi proposto mostrou ser efetivo, contribuindo para uma melhor reprodutibilidade dos revestimentos quando se pretender utilizar solventes orgânicos que promovam inchamento da membrana.

Declaração

Declara, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

Assinar e datar

Table of contents

Notation e glossary

K_2	example of a variable with *subscript*
K_2^T	example of a variable with *subscript* and *upperscript*
K^T	example of a variable with *upperscript*

Greek letters

ε	dielectric constant	
ρ	density	Kg m^{-3}
μ	viscosity	Pa s^{-1}
i	current density	A m^{-2}
Ω	electric resistance unit (ohm)	Kg m^2 s^{-3} A^{-2}

Abbreviations list

PEM	Polymer Electrolyte Membrane or Proton Exchange Membrane
MEA	Membrane Electrode Assembly
CCM	Catalyst Coated Membrane
CCS	Catalyst Coated Substrate
GDL	Gas Diffusion Layer
GDE	Gas Diffusion Electrode
PTFE	Polytetraflruoroethylene
PFSA	Perfluorosulfonic acid
EIS	Electrochemical Impedance Spectroscopy
OER	Oxygen Evolution Reaction
HER	Hydrogen Evolution Reaction

1 - Introduction

1.1 - Framework and project description

Nowadays hydrogen is mostly produced by methane reforming; but it would be an optimal energy carrier if produced from renewable sources. As an alternative, among the so-called low temperature processes, hydrogen can be electrochemically produced. Water can be split into hydrogen and oxygen by passing an electrical current through electrochemical cells. Through this process, the quality of the produced hydrogen is much higher when compared with the one obtained from fossil fuels. Electrochemically produced hydrogen can be used to store the surplus from renewable energy sources.

Though many different types of electrolyzers exist, all of them have in common the configuration with two electrodes and an electrolyte. Usually electrolyzers are classified by the type of electrolyte material and the operating temperature. Alkaline and Polymer Electrolyte Membrane (PEM) water electrolysis are nowadays the more mature existing electrochemical technologies for production of hydrogen [1].

PEM electrolysis investment cost is higher than alkaline electrolysis. It allows nonetheless operation at much higher current densities (up to 2 A cm^{-2} while alkaline electrolysis provides current densities typically around 0.3 A cm^{-2}) [1], with a significant potential for cost reduction owing to the compact system design. A solid polymer electrolyte is used in PEM cells. Both sides of the membrane are coated with a thin layer of material containing precious metal catalysts (platinum, palladium, iridium and ruthenium are the most common examples). One side of the MEA will act as anode and the other side as cathode. The configuration of the two electrodes with the membrane is known as Membrane Electrode Assembly (MEA).

In a Hydrogen Energy Society scenario, PEM electrolyzer catalyst costs need to be reduced by 50 % until 2017 [2]; this could be achievable by reducing catalyst loadings and developing coating methods for mass production of MEAs. Mainly, this is due to the availability of precious metal catalysts and the need for higher reproducibility of the coating process.

Wet routes for fabrication of MEAs, such as screen printing method, have great potential for cost-effectiveness and good reproducibility when compared to other coating methods like decal, spraying, piezoelectric film deposition, etc. The aim is to provide durability and high performance to the cell with low precious catalyst loadings through a well-established, scalable and fast coating process. For this purpose, screen printing can be used to produce catalyst coated membranes (CCMs), where the catalyst loading is directly applied on the membrane [3].

The goal is to develop a CCM able to fulfill activity and durability performance targets for potential industrial production of MEAs. Composition of the paste, fabrication procedure, characteristics of the membrane will have a critical impact on the goals mentioned before. Both variables and goals are intrinsically dependent with each other. This work focuses on the development of MEAs for PEM electrolysis by screen printing, covering different aspects ranging from the materials science for the ink formulation and production, the coating methodology and the subsequent morphological characterization, to electrochemistry for the assessment of the MEAs performance by means of electrochemical impedance spectroscopy (EIS) and current/potential characterization along time.

1.2 – Hosting Institution

DLR (Deutsches Zentrum für Luft und Raumfahrt) at Stuttgart has its origin in the Research Institute of Jet Propulsion Physics, established in 1954 at Stuttgart airport. Since 1961, the site has been located in the Pfaffenwald in Stuttgart-Vaihingen. As a result of its geographic proximity to the University of Stuttgart, together with the close collaboration in research and education, the DLR site has become an important part of the scientific community in Stuttgart.

DLR has more than 700 employees in six institutes at the DLR site in Stuttgart. The main research areas include high performance structures made from ceramic fiber, polymer and hybrid composites, innovative road and rail vehicle concepts, laser system development, energy storage and conversion technologies, gas turbines and combustion processes and the development of receivers for solar power plants. The research conducted here is supported by an extensive infrastructure with unique test rigs and large-scale research facilities.

The Institute of Engineering Thermodynamics at DLR in Stuttgart, with further research facilities in Cologne, Ulm and Hamburg, does research in the field of efficient energy storage systems that conserve natural resources, and next generation energy conversion technologies with a staff of 150 scientific and technical employees, engineers and doctoral candidates.

The spectrum of activities ranges from theoretical studies to laboratory work for basic research and to the operation of pilot plants. These experimental and theoretical studies are accompanied by systems analysis studies to analyze the associated technological, environmental and economic potential and situate it in a larger overall context of the energy economy by means of scenarios.

The section Electrochemical Energy Technology, a team of about 60 persons, develops efficient electrochemical storage and conversion devices, namely electrolyzers, fuel cells, and advanced batteries. These technologies are becoming more important in future energy systems due to the transformation of the energy sector in Germany. Those activities range from materials development, cell design, stack development, manufacturing and advanced diagnostics up to

system optimization. For specific innovative applications demonstrators and prototypes are developed. Scientific and technical challenges for electrochemical energy technology include finding solutions to conflicting goals of efficiency, durability, safety, reliability and cost reduction.

1.3 – Work contributions

DLR intends to demonstrate until 2019 cost effective PEM electrolysis with a low catalyst loading. As an easily up-scalable technique, with possibility of continuous processing, the screen printing coating technology is believed to be a suitable technology for producing MEA with low loading of catalysts.

Nowadays, DLR does not own a proprietary technology for producing highly efficient MEA for PEM electrolysis. Moreover, looking at the literature, there is still a lack of understanding regarding the behavior and the performance of electrode with catalyst loading below 1 mg cm^{-2}.

With the perspective of this mid term demonstration goal of PEM electrolysis, this work contribute in mainly two aspects:

- Assess the screen printing technology potential for producing high efficient MEA for PEM electrolysis, with a good reproducibility;
- Assess the performance and investigate degradation issues, which might be specifically correlated with the coating technology.

There are several advantages in producing own MEAs, like being able to control electrocatalysts, catalyst loadings, electrodes thicknesses and Nafion ionomer content in the catalyst layers. A coating technique with high reproducibility and high scalability can be a powerful scientific tool for DLR's PEM electrolysis scientific research.

1.4 – Thesis organization

This thesis is divided in five chapters: Introduction, State-of-the-art, Materials and methods, Results and discussion, and Conclusion.

In the first chapter, introduction, the project is framed and described, followed by an introduction of the hosting institute and mentions of the contributions of this work not only for DLR but also to the scientific community. In the second chapter is presented a literature research about the state-of-the-art of considered technologies and techniques. In materials and methods chapter is described all the experimental work that was performed. Results are shown and discussed in the

fourth chapter and the final chapter contains all the considerations that could be concluded in the end of this project.

2 - State-of-the-art

2.1 - PEM electrolyzer

2.1.1 – Basic principles of operation

An electrolyzer is an electrochemical device that converts electrical energy in chemical energy, splitting water and releasing hydrogen, oxygen and heat. Mainly, electrolyzers can be classified by the operation temperature and type of electrolyte. Among low temperature electrolyzers, proton exchange membrane (PEM) electrolyzer (uses solid acid membranes) is mostly preferred due to ease of handling and safety. This is due to the possibility of operating with a wider range of current densities when compared with alkaline electrolyzers. PEM electrolyzers are capable of achieving values of current density above 2 A cm^{-2}. This reduces operational costs and potentially the overall cost of electrolysis. Several losses limit maximum achievable current densities (activation, ohmic and mass diffusion losses). With a thin membrane, capable of providing good proton conductivity (*ca.* 0.1 S cm^{-1}), high current densities can be achieved [1]. As PEM electrolyzer produces high purity hydrogen and oxygen (≈99.999 %), there is no need of another purification step [4].

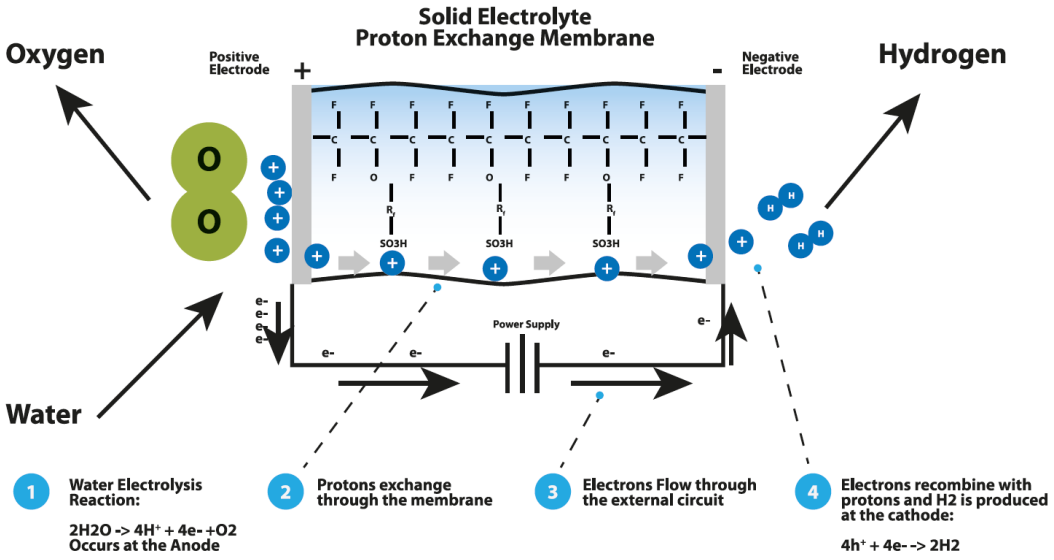


Figure 1 - Illustration of PEM electrolysis basic principles (extracted from [5]).

Figure 1 shows the principles of operation of an electrolyzer. It shows the main physical and chemical processes that occur in a MEA during water electrolysis. Pure water is oxidized to oxygen in the anode, producing protons and electrons. Hydrated protons ($H^+.xH_2O$) migrate to the cathode through the membrane, where they recombine electrochemically with electrons, producing hydrogen [6].

The overall reaction is shown below:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad (1)$$

Specifying the reaction in each electrode, in the anode occurs the water splitting:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \quad (2)$$

Hydrogen reduction happens in the cathode:

$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

2.1.2 – Thermodynamics

The equilibrium cell potential at standard temperature and pressure (E^0) is 1.23 V and can be related to the Gibbs free energy (ΔG) of the electrochemical reaction, as shown below [7].

$$\Delta G = -nFE^0 \quad (4)$$

where n is the number of electrons transferred in the reaction and F is the Faraday constant (96 486 C mol^{-1}). Gibbs free energy of a chemical reaction changes with temperature, pressure and concentration. Therefore, the open circuit potential (OCP) at a given temperature and pressure can be found by Nernst equation:

$$E = E^0 + \frac{RT_{cell}}{2F} ln \frac{P_{H_2} P_{O_2}^{1/2}}{a_{H_2O}} \quad (5)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T_{cell} is the cell temperature, P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen and a_{H_2O} is the activity of water.

The cell potential required to drive the reaction forward is greater than the thermodynamic value as there are various resistances (losses) involved in the system. The overpotential caused by resistances is converted into heat.

The efficiency of an electrolyzer cell is highly dependent on the respective operating conditions. PEM electrolysis cells have efficiencies between 55 % - 70 % [8]. The efficiency of any energy system can be defined as [9]:

$$\eta = \frac{\text{useful energy obtained}}{\text{energy available for conversion}} \quad (6)$$

There are a number of ways of expressing electrolyzer efficiency, depending on the way the system is assessed and compared. The electrical efficiency, η can be expressed as shown in Equation 7 [10]:

$$\eta = \frac{W_{H_2}}{W_{el}} \tag{7}$$

where W_{H_2} is the generated chemical energy and W_{el} is the required electrical energy. These terms can be expressed as shown in Equation 8 and 9.

$$W_{H_2} = \dot{N}_{H_2} H \tag{8}$$

$$W_{el} = EIt \tag{9}$$

where $\dot{N}_{H_2}$ is the molar rate of produced hydrogen, H is the heating value for hydrogen, E is the potential, I is the current and t is the time [6].

2.1.3 – Electrolyzer assembly structure

Figure 2 shows a typical assembly of a PEM electrolyzer. Although some other configurations are possible, the most important features are clarified in the scheme. The typical assembly components of a PEM electrolyzer cell consist in a MEA, current collectors and bipolar plates.

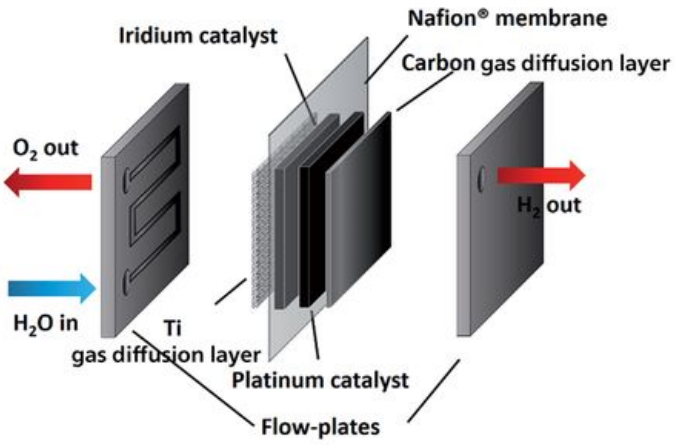


Figure 2 - Illustration of a PEM electrolyzer cell general structure (extracted from [3]).

Regarding the current collectors materials, cathode and anode have different demands. At cathode side, potentials are close to zero, though it is possible to use carbon-based materials already known in PEM fuel cells. But these materials are not stable at anode's working potential (*ca*. 2 V). Carbon undergoes electrochemical oxidation at potentials higher than 0.9 V. Porous titanium structures are mainly used. The main drawbacks of these materials are the formation of oxide layers and high cost [12]. Requirements for bipolar plates in PEM electrolysis also differ from the ones for PEM fuel

cells thanks to the oxidizing environment at the anode. In this case, titanium plates (or coatings) can replace carbon plates, because it forms a passivation layer rendering its resistance to corrosion. These plates can be coated with platinum to prevent formation of the titanium oxide layer that increases ohmic resistances [13].

The catalyst coated membrane (CCM) has two electrocatalyst layers, where hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) take place. They are bonded to the membrane while maintaining its porosity to reduce mass transfer resistances [14]. Typically, platinum black or palladium black, carbon supported platinum or palladium nanoparticles are used in the cathode side thanks to their high activity for the HER [15,16].

OER governs the efficiency of water electrolysis as most of the overpotential losses are related to the electrochemical processes at the anode [17]. The acidic environment and high anodic overpotential created during water electrolysis make highly challenging the use non-noble metals like Ni and Co as the anode electrocatalyst due to corrosion [18]. Based on these requirements, iridium oxide (IrO_2), ruthenium oxide (RuO_2), a mixture of the two oxides and platinum iridium (PtIr) are commonly used anode electrocatalysts [19]. Iridium (or IrO_2) is generally recognized as the state-of-the-art for the OER in PEM electrolysis. Ruthenium (or RuO_2) is more active and cheaper than IrO_2, but problems related to instability at high potentials (like corrosion) limit its use [17]. A cost effective nanostructured Ir-supported on Ti_4O_7 is also available as electrocatalyst for the anode. It outperforms the commercial iridium black in terms of mass activity for the OER in acid medium, allowing reduction of precious metal loading by taking advantage of the use of the electro-ceramic support [20].

2.1.4 – PEM electrolyzer performances in literature

It is difficult to compare PEM electrolyzer performances because they are highly dependent on the assembly components and the operation conditions. Anode catalyst, catalyst loadings and cell temperature are the most relevant variables. Current collectors material is also very important, mainly for durability issues. Table 1 reviews the most recent PEM electrolyzers, including their potential at 1 $A \cdot cm^{-2}$.

Table 1 – *Review of the most recent PEM electrolyzers*.

Reference	Anode catalyst	Cathode catalyst	Anode loading mg cm^{-2}	Cathode loading mg cm^{-2}	Anode CC	Cathode CC	Cell temperature (°C)	*E* (V) @ 1 A cm^{-2}	Coating method
[21]	IrO_2	40%Pt/C_{JM}	1	0.2	C Cloth	C Cloth	80	1.64	Decal
[22]	Ir Black	40%Pt/C_{XC72}	1	0.8	SPT	SPT	90	1.7	-
[23]	Ir Black	Pt	2.5	1	SPT	SPT	90	1.79	S-SPT
[24]	IrO_2	30%Pt/C_{TKK}	1.5	0.5	C Toray	C Toray	80	1.67	S-Mem
[25]	Ir Black	Pt Black	2	0.8	Pt/SPT	Pt/SPT	90	1.71	S-SPT

Abbreviations: TKK=Tanaka Corp.; JM=Johnson & Matthey; SPT=sintered porous titanium; C=carbon; S=sprayed catalysts; Mem=membrane; CC=current collectors.

2.2 - MEA fabrication

2.2.1 – Fabrication strategies

There are two main strategies to prepare a MEA. The first is to produce a catalyst coated membrane (CCM-MEA); as the name suggests, the catalyst layer is coated on the membrane. The second approach is to make catalyst deposition on the conductive support - catalyst coated substrate (CCS). When the CCSs are assembled with the membrane, this assembly can be called as gas diffusion electrode (GDE-MEA). The first MEA type is considered a three-layer assembly, while the second type is a five-layer assembly [26].

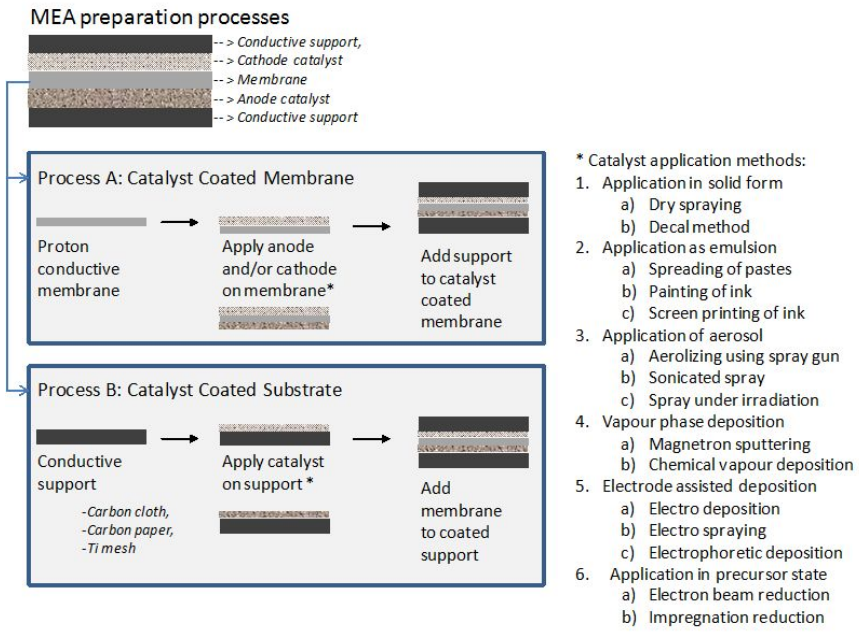


Figure 3 - Scheme of MEA preparation process alternatives (adapted from [27]).

In principle, paste deposition on the membrane (CCM) will provide better attachment between the electrode and the electrolyte, providing a zero-gap concept. A lower contact resistance, between the electrode and electrolyte results in improved MEA performance. The better attachment of the catalyst layers to the membrane not only reduces ohmic resistances in the interface but also provides better mechanical stability [27].

In order to produce CCMs there are two different approaches: direct and indirect coating of the membrane; direct coating can make the membrane to swell thanks to the contact of it with organic solvents. Membrane swelling can lead to poor dispersion and uneven coating. With decal-transfer (indirect coating), the catalyst layer is coated on a substrate (such as Teflon or polyamide) and, after drying, it is transferred to the membrane via hot press. However this can cause losses of catalyst during the transfer process. [27]. Hot press parameters (temperature, pressure, time) have great influence on the performance of the developed MEAs. Hot pressing is the most common procedure to improve the contact between the layers [3].

As shown in Figure 3, there are various coating methods to prepare both types of MEAs. The most commonly applied methods are spraying [28]; and blade coating based methods [29]. The choice depends on several factors such as scalability, reproducibility and type of application.

2.2.2 – Polymer electrolyte membrane

Polymer electrolyte membranes, in state-of-the-art technology, are perfluorinated membrane materials, such as Nafion®. These materials gather most of the important properties needed to perform PEM cell operations: they offer high protonic conductivity, and high mechanical and electrochemical stability [30].

These materials have three distinct features:

- Polytetrafluoroethylene (PTFE) acting as a backbone structure (hydrophobic region);
- Ether-linked side chains of varying length and flexibility that connect PTFE backbone to the acidic region;
- Sulphonic acid moieties (hydrophilic region).

A schematic of the polyfluorosulfonated acid (PFSA) molecular structure is presented in Figure 4:

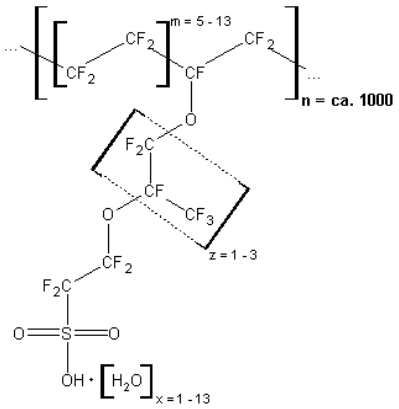


Figure 4 – Schematic of PFSA molecular structure (extracted from [31]).

Upon hydration of the membrane, protons from the sulfonic acid group become mobile as hydronium ions, allowing their movement between the sulfonic acid sites [32]. Mobility of protons under good humidification conditions translates to a very low voltage drop due to ohmic resistance, approximately 20 mV at 1 A cm^{-2} [26].

Nafion® membranes are available in several thicknesses that can be chosen depending on the type of application. Thinner membranes provide less conductivity resistances but this will compromise mechanical stability and selectivity, when compared to thicker membranes.

Lately, Nafion® membranes have a "CS" – chemically stable classification. These membranes have improved chemical stability that increases durability. For this, stabilizers (low molecular molecules) are added to the PTFE backbone, improving the bonding between monomers and fluoride groups [33].

When Nafion® absorbs water, that sulfonated groups are redistributed making membrane to swell; the numeric density of sulfonated groups falls. The degree of Nafion swelling in a pure solvent is related to its polarity for both protic and aprotic solvents. In general, the uptake of polar solvents exceeds that of non-polar for the pure solvent case. However, when water is combined with a solvent, the degree of swelling is inversely related to the polarity of the solvent [34,35,36].

Some mechanical techniques are employed to prevent/minimize swelling (vacuum system and rubber frame are two examples). In order to prevent it, there is a chemical procedure that consists in changing the protonic (H^+) to Na^+ form of Nafion before coating the membrane, and in MEA reprotonation after the coating process [3].

2.2.3 – Catalyst layers

Manufacturing of electrocatalyst layers constitute an important phase for determining the whole performance of PEM cells. These layers are the key component in MEAs because it is where

electrochemical reactions take place. The ideal catalyst layer should provide high catalyst utilization, high durability, high electronic conductivity and high mass transport capacity [1].

In order to enhance the triple phase boundary (Figure 5), an ionomer is added to the catalyst layer. This is a solubilized form of the membrane that extends proton conduction paths into the porous diffusion layer structure, connecting more catalyst sites to the membrane.

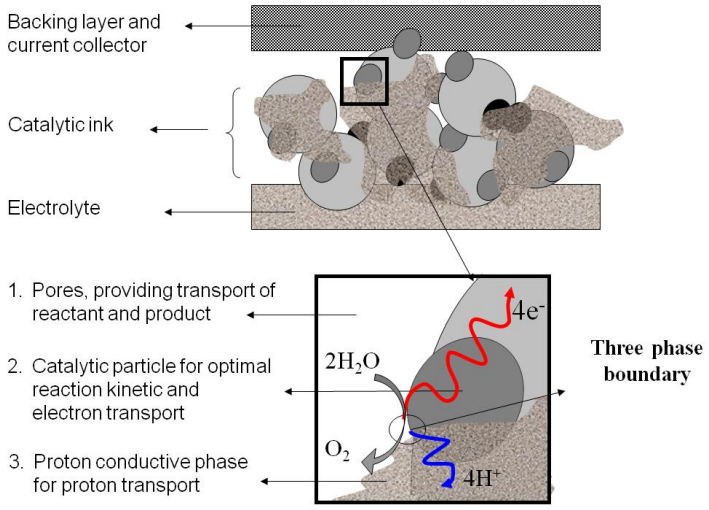


Figure 5 – Illustration of the triple phase boundary system (extracted from [37])

Proper dispersion of Nafion® ionomer and catalyst particles is critical for MEA's power density and catalyst activity. Thereby the selection of solvents, used in the inks/pastes, is a key factor in the preparation of the catalyst layer. MEA preparation routes have significant effects on the microstructure and therefore in electrochemical properties of the catalyst layer. This has to do with the molecular interaction between Nafion® ionomer and used organic solvent [37].

2.2.4 – Screen printing method

Four items are essential for screen printing of MEAs: printing medium (catalyst ink or paste), a substrate onto which the print will be made (conductive substrate or proton exchange membrane), a screen to define required patterns and a squeegee to force the paste through the screen [27].

In this method, a screen (or sieve or mesh) is held above the substrate, while pre-prepared catalyst ink is applied over it. The screen is brought into contact with the membrane by the squeegee as it is moved over the screen. The ink is pushed into the open area forming the pattern, depositing it on the membrane and its surplus is removed by the edge of the squeegee.

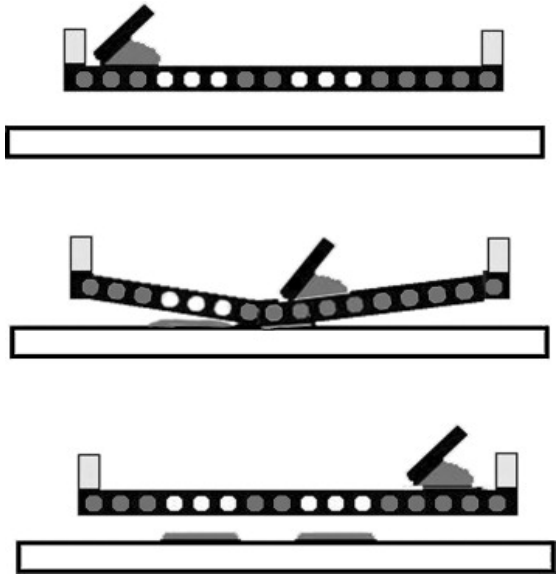


Figure 7 - Screen printing schematic illustration (extracted from [53]).

The print matrix consists of a mesh of (metallic or polymeric) wires. The free volume, for paste penetration, can be controlled by the mesh count [38]. The pore size in the screen must be optimized to be greater than the particle size of the catalysts to get an optimum print quality. The mesh defines the wet coating thickness. Therefore, in order to precisely control catalyst loadings, three parameters should be considered: ratio between solid particles and solvent in the paste; mesh porosity; number of deposited layers in each electrode.

The limitation of this method is that larger particles tend to get clogged and could produce irregularly printed patterns on the substrate surface. Thanks to this limitation, flow properties of the material (viscosity and its change under mechanical stress) are very important. Thereby, characterization of the flow properties allows optimization of the printing process [39].

In order to evaporate organic solvents from the coated membranes, several procedures are reported in the literature. They suggest more or less intensive drying (higher temperatures with less drying time or lower temperatures with more drying time). The main goal is that the solvent can be considered totally evaporated from the coated layer without damage of the MEA.

2.2.5 – Recipes and Paste Preparation

This is a crucial step in the fabrication of the MEAs. In case of preparing pastes/inks for screen printing technique, it is required high reproducibility regarding the processing. With this coating technique, this is guaranteed only if the prepared paste is homogeneous and with desired flow behavior. Although several different types of pastes can be processed with screen printing method,

the mechanical behavior of the paste is decisive. It is possible to quantify many parameters (viscosity, surface tension, solid content of the paste and homogeneity) that will conduct to the right behavior, but they can change if the materials differ from paste to paste.

Since presented the idea of using solubilized Nafion® in catalyst inks/pastes it has been widely accepted and used for high-performance MEAs fabrication [40]. Along with this solution, precious metal catalysts are added, sometimes with support (carbon nanoparticles, titanium oxides are some examples) or with some more complicated configurations (sintered or core-shell structures) in order to provide electrochemical activity and stability. Mixing these two ingredients (ionomer and catalyst or supported catalyst) with organic solvents is the pre-requisite for producing good CCMs. Sometimes additives (plasticizers, silica, etc.) can be added for providing special properties to the produced MEAs.

Generally, a good solvent choice should satisfy three criterions: viscosity, evaporation rate and relative permittivity (or dielectric constant). Clumps or cracks could often be seen on the catalyst layers from pastes with to less viscous solvents. On the other hand, if a solvent is too viscous, adhesion of the catalyst layer to the membrane will be very weak. A suitable solvent or a combination of solvents for the screen printing paste should be in the range of 16×10^{-3} Pa $s^{-1} < \mu < 60 \times 10^{-3}$ Pa s^{-1} [3]. Regarding evaporation rate, it should be low because a long handling life is needed. If a solvent evaporates too fast, the paste might become very dry even before application on the membrane. At the same time, it should not be too low otherwise drying time would be too long to obtain high manufacturing throughput [3]. Dielectric constant or relative permittivity (ε) is a relative measurement of a solvent polarity. This property has influence on Nafion® ionomer distribution along the catalyst layer [41]. Organic solvents with $\varepsilon < 3$ make Nafion® particles to precipitate and agglomerate. Organic solvents with $3 < \varepsilon < 10$, make those particles stay in "colloidal" form. If dielectric constant is above 10, Nafion® will be in solution form, allowing better triple-phase-boundary conditions [42].

2.3 - Electrochemical Characterization Tools

2.3.1 – Polarization Curve

The polarization curve is an important characteristic of PEM cells, because data record is made under operating conditions similar to those of real applications. It displays potential difference between the two electrodes as a function of the current passing through a variable resistive load. This curve allows quantification of the fundamental properties of the cell, if current is normalized to electrode's area [43].

Polarization curve for a single PEM cell has three major regions, as shown in Figure 7. Very often, polarization curves are converted to power density versus current density, by multiplying potential by current density in each point of the curve. The plot of power density versus current density can directly show nominal and maximum power of the cell. Steady-state polarization curve can be obtained by recording current as function of cell potential or vice-versa [43].

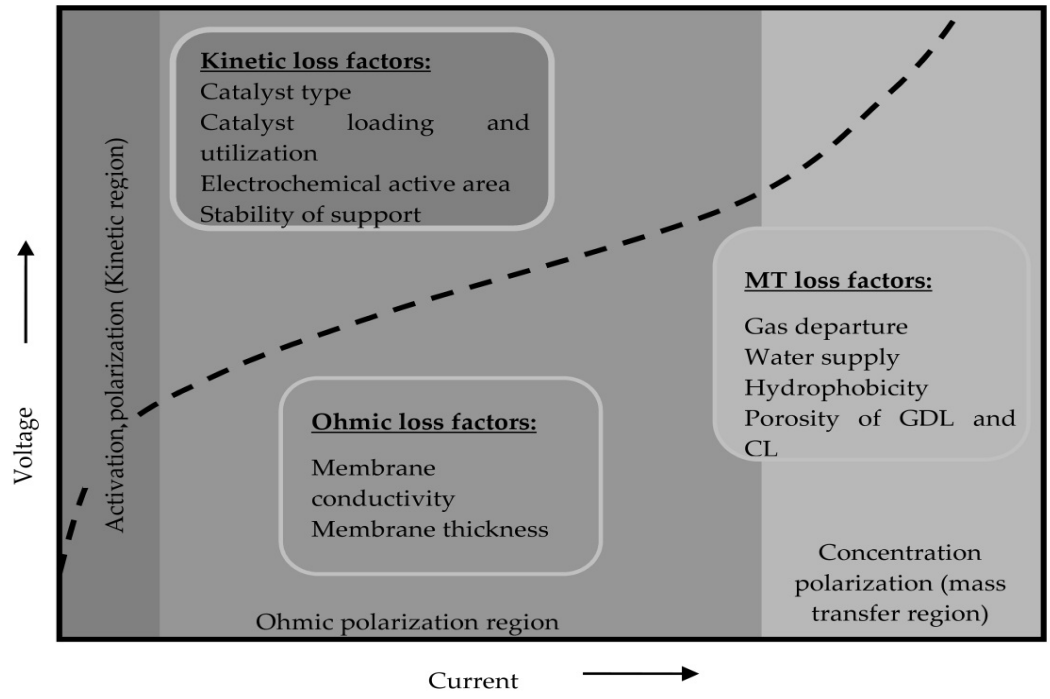


Figure 7 - Polarization curve of an electrolyzer (extracted from [27])

In Figure 7, it is easy to notice three main types of potential losses that occur in an electrolyzer. Concerning the activation polarization region, potential losses happen due to kinetic factors, mainly because of the sluggish kinetics of OER. At intermediate current densities (ohmic polarization region), there can be potential losses thanks to resistances in flow of protons through the electrolyte and resistances in flow of electrons through the electrodes. In ohmic polarization region, potential losses are linear with current density, while activation overpotential reaches a relatively constant value. At high current densities (concentration polarization region), mass transport effects dominate, mainly due to transport limitations, through porous structure of diffusional and catalytic layers, of reactant (feed) and gas products (removal).

It is also interesting, for MEA's performance characterization, to introduce time as a variable. Thereby, considerations about durability of the MEA can be made. To introduce time as a variable, it is necessary to perform potentiostatic (fixed potential) or galvanostatic (fixed current density) polarizations and record current density or potential, respectively, along time.

2.3.2 – Electrochemical Impedance Spectroscopy (EIS)

EIS is a technique whereby electrochemical system is characterized by applying a sinusoidal perturbation of the potential (potentiostatic mode) or the current (galvanostatic mode) over a range of frequencies and observing the electrical response. By introducing a frequency domain over a range from mHz to MHz, processes on different time scales, from instantaneously to one minute, can be decoupled. EIS is mainly an in-situ technique to diagnose cell properties and performance.

One convenient method to analyze EIS data is by interpreting the frequency response through an equivalent circuit model. This model represents the dominant electrochemical and fluid dynamic factors in combinations of capacitors, inductors and resistors [44].

Charge transfer interfaces are modeled using a parallel connection of a polarization resistance with a constant phase element [45]. Constant phase elements are used to take into account deviations of double layers from ideal capacitive behaviors due to surface roughness, polycrystalinitty and anion adsorption. Diffusion impedances are added in series to account for possible mass transport limitations of hydrogen and oxygen gases away from the interfaces across current collectors. Interface impedances are also series connected to ohmic resistances to consider electronic and ionic conductivity of cell components [46].

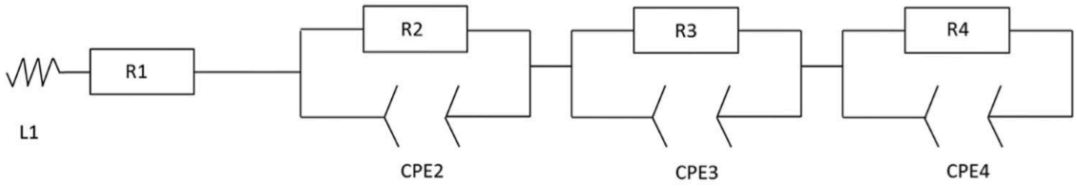


Figure 8 - Equivalent circuit of a PEM electrolyzer for simulating EIS data (extracted from [47])

In figure 8, R1 and L1 correspond to the resistance associated to the interconnecting elements and membrane. R2 and CP2 are associated with charge transfer resistances at the interface of the diffusion layer and the catalyst layer. Kinetic resistance of the oxygen evolution reaction is represented by R3 and CP3. Finally, R4 and CP4 represent mass transport limitation effects that can occur at high current densities [47].

3 - Materials and Methods

3.1 – Coating materials

The chosen electrolyte was Nafion® NRE-212 CS membrane from Chemours™ (owned by DuPont™). This reference addresses a thin membrane (approx. 51 μm of thickness) among Nafion's catalogue. Regarding the electrodes, four types of materials were used in order to produce a coating system: catalyst, support, binder and solvent. For the cathode catalyst, Pt/C was chosen. For the anode, two different types of catalyst were used in two different moments: a confidential structure of supported iridium and a mixture of iridium black with Ti_4O_7 as catalyst and support, respectively. As a binder, Nafion® ionomer solution was used. A mixture of water and low weight alcohols solubilizes the ionomer particles. Regarding the organic solvent that finishes the paste composition, four different solvents were studied: α - terpineol; ethane-1,2-diol; propan-1,2-diol and cyclohexanol.

Table 2 – Materials used in catalyst inks for screen printing method

Material	***Function***	***Supplier***
20% mass of Pt/C	Supported catalyst	E-TEK, 1998
HISPEC 60% mass of Pt/C	Supported catalyst	Johnson Mathew, 2015
Supported Ir	Supported catalyst	Umicore, 2015
Ir Black	Catalyst	-
Ti_4O_7	Support	-
20% mass of solubilized Nafion® ionomer	Binder	Sigma-Aldrich, 2015
5% mass of solubilized Nafion® ionomer	Binder	Ion Power, 2016
α - terpineol	Solvent	Alfa Aesar
Ethane-1,2-diol	Solvent	Sigma Aldrich
Propan-1,2-diol	Solvent	VWR, 2015
Cyclohexanol	Solvent	VWR, 2015

3.2 – MEA fabrication

3.2.1 – Paste preparation for screen printing method

Different paste compositions were prepared. Some parameters were kept constant and others did not, according to the aim of each study. In all prepared pastes, ratio between Nafion® particles (from Nafion® solution) and the total of solid particles in the paste was kept at 30 % by mass. Mixture and milling of catalyst powder with Nafion® solution and chosen organic solvent was performed in two different ways: first using a 3-roll mill machine EXAKT 80E EL, and then using a mortar and a pestle. The solvents from the Nafion® solution were evaporated while mixing and milling. Only then, the chosen organic solvent was added.

Among pastes that were prepared with mortar and pestle, solid content in the pastes was between 35 %-40 % by mass. But if the paste was mixed with the roll mill machine, the solid content was decreased to 25 % by mass. Regarding the catalyst powders used for the anode, two different catalysts were used: a confidential supported iridium catalyst and a mixture of iridium black and Ti_4O_7 (30 % Ir by mass). For the cathode, Pt/C (20% Pt by mass) was used.

The paste prepared with cyclohexanol as solvent requires one processing particularity. While pastes with the other solvents were prepared at room temperature, cyclohexanol had to be heated to 30 °C in a water bath. Under normal pressure, melting temperature of cyclohexanol is 18 °C. When stored, the solvent is solidified. Coatings with this paste were performed immediately after paste preparation, trying to keep the paste properties intact.

3.2.2 – Screen printing method

Nafion® membranes were cut in squares of 49 cm^2. After removing the protection foils and weighted, they were put over a porous metal substrate (with 25 cm^2) that was attached to the screen printing table. The vacuum system of the machine was used to avoid any movement of the membrane during the coating process. A screen printer 900 from Aurel® was used for the coating procedure with a Koenen® Typ-10 M6 mesh with opened area for coating of 25 cm^2. The printing pressure, between squeegee and mesh, was 1.5 N cm^{-2}. The distance between the screen and the membrane was set to 80 mm.

The coated membrane was dried, still with the vacuum system on, with a lamp for 10 minutes. The drying procedure was completed in a hoven for 20 minutes at 75 °C. After 2 hours, the coated membrane was weighted again in order to calculate its catalyst loading. After coating and drying the MEA, it was hot pressed. It was put inside two PTFE sheets and then, all together, between two steel plates. The parameters that were used for hot press were:

- Pressure: 17.5 bar;
- Temperature: 125 °C;
- Pressing time: 5 minutes.

Each prepared CCM was kept in a plastic bag, numbered for identification issues and stored in a MEA portfolio.

3.2.3 – Wet spraying method

This coating method was only used to produce cathode catalyst layers. It was performed always after screen printing anode layers. A catalyst suspension was prepared mixing Pt/C (60 % Pt by mass) with solubilized Nafion® particles (5 % Nafion® by mass). The mass ratio between Nafion® particles and the total of solid particles was 35 %. Additionally with the solvents that come from Nafion® solution, it was added a mixture of water and isopropanol in a 1:1 proportion. Water was the first solvent to be added to Pt/C powder in order to prevent ignition of nanoparticles when in contact with an organic solvent. The solid content of the suspension is 0.8 % by mass. The suspension was mixed with an ultrasonic bath mixer with ice.

The catalyst suspension was sprayed, calculating the sprayed amount to reach the aimed catalyst loading (10% losses were assumed with this coating method). Per cathode layer (with 4 cm^2) it was used 400 µl of suspension, leading to a catalyst loading of 0.5 mg cm^{-2}. Temperature of the vacuum plate was set at 105 °C. Sprayed membranes always followed to hot press step.

3.2.4 – Membrane swelling treatment

Performing the swelling treatment reported in [3]; after cutting Nafion® membranes, they were boiled in $NaOH_{(aq)}$ 0.25 M for 15 minutes. After changed H^+ to Na^+ ionic form, membranes were washed and boiled in deionized water for 10 minutes and followed the normal printing procedure. After coated, dried and hot pressed, membranes were boiled in $H_2SO_{4\ (aq)}$ 0.5 M for 30 minutes in order to reconvert to protonic form. Then they were rinsed three times in deionized water to remove any acid traces.

3.2.5 – Pre-treatment of the membrane

Following part of the work reported in [48], two membranes were boiled for 30 minutes in mineral acids for protonation form improvement. One of them was boiled in 0.5 M sulfuric acid. The other

membrane was boiled in 0.5 M nitric acid. Both membranes were then rinsed and boiled in deionized water. The pre-treated membranes followed to coating procedure as usual.

3.3 – Electrolyzer assembly

In order to perform electrochemical tests to the produced MEAs, two different cell sizes were used. They differ not only on the cell size but also on different current collectors/diffusion layers. Steel bipolar plates had a polymer coating to hinder current conduction through undesired area. Both cells were coupled with a temperature control system and connected to a potentiostat for current supply. The electrolyzer cell was submerged in a glass container with ultra-pure water. Produced hydrogen and oxygen were released to an exhaustion system. MEAs for each cell size, were intentionally cut with a small extra area, in order to prevent touching of the current collectors, that would cause a short circuit. The specific characteristics of two cell assemblies are:

1 cm^2 cell - the MEA stands between two current collectors made of sintered porous titanium. Ice Cube Sealing 35 FC-PO 100 gasket was used to center the MEA and current collectors in the middle of the bipolar plate. The gasket was cut with a frame shape, with a hole of the size of the current collectors, allowing them to contact directly with the bipolar plate. The assembly was fixed with a clamp. Two PTFE sheets were used, between the clamp and bipolar plates, in order to delay corrosion of the clamp.

4 cm^2 cell - current collectors differ from the ones used in the 1 cm^2 cell. At anode side, a titanium mesh was used between the bipolar plate and a sintered porous titanium current collector that is coated with Pt. At cathode side, the diffusion layer/current collector was a junction of three Toray papers 030. In order to hold the cell together, four screws were used instead of the clamp. In the water container there was an ionic exchange resin for water purification. Any gasket was used with this cell size assembling.

4 – Results and Discussion

Electrochemical results are divided in two parts. In the first part the 1 cm^2 cell was used, with an Ir mixture as anode catalyst and operation potential of 2 V. In the second part the 4 cm^2 cell was used, with supported Ir black in Ti_4O_7 and operation potential of 1.7 V. Without explicit mention, all electrochemical tests follow the chronology of the project. This chronology is relevant for results interpretation, because some posterior electrochemical tests were made taking into account previous tests.

Regarding the electrochemical behavior of the tested cells, they are shown through potentiostatic polarization plots and electrochemical impedance spectroscopy Nyquist plots. Electrochemical results are shown with absolute values and not normalized by the active area. Because durability issues are very important in the framework of this project, it is very relevant to plot the cell behavior along time. Therefore, a value for potential was fixed and current was plotted over time - potentiostatic polarization. Potentiostatic polarization was chosen instead of galvanostatic polarization in order to try to keep cell degradation as linear as possible. EIS technique is not as well established for PEM electrolyzers as it is for other electrochemical cells. Still, it can be helpful on corroborating polarization behavior of the MEAs or assess different types of resistances and their contribution to the total cell resistance (even when those resistances cannot be identified).

4.1 – First part of electrochemical tests results

The developed MEAs had both electrodes coated with screen printing method. The chosen electrocatalysts were supported iridium catalyst from Umicore® was used in the anode while Pt/C (20% Pt by mass) was used in the cathode. Catalyst inks were prepared using α - terpineol as solvent. The catalyst loadings were 2 mg cm^{-2} of Ir and 0.8 mg cm^{-2} of Pt in the anode and cathode, respectively. An experimental MEA from Solvicore® (with Ir and Pt as anode and cathode catalysts, respectively) was electrochemically tested for comparison issues. Without explicit specific mention, electrochemical tests in this first part were performed in potentiostatic mode at 2 V and at 20 °C.

4.1.1 – Electrochemical activity influence of MEA extra area

Although the cell that was used had 1 cm^2 of area, MEAs had to be cut larger than the nominal area to prevent the two electrodes to short-circuit. Two square pieces, of an experimental MEA from Solvicore®, were cut with different extra areas.

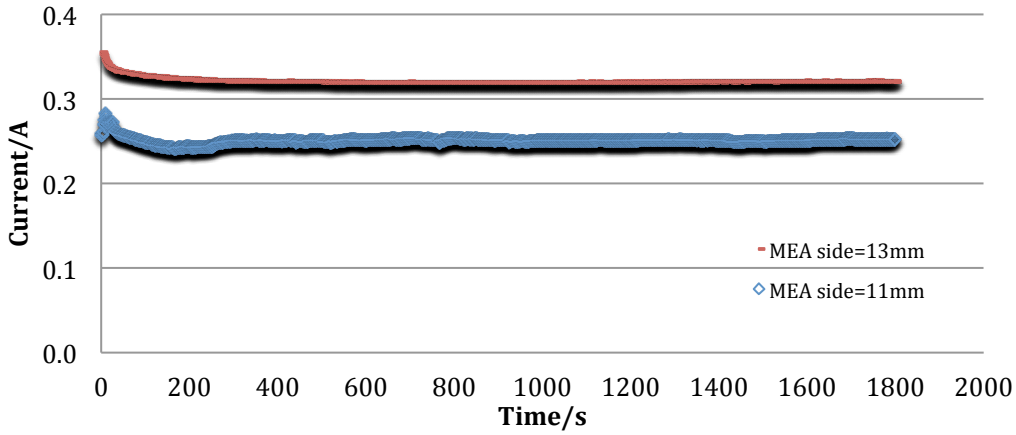


Figure 9 - Potentiostatic polarization curves illustrating influence of MEA (from Solvicore®) size in cell activity. Performed at 2 V and 22 °C.

In Figure 9, larger area MEA shows more activity than the smaller area MEA. Catalyst layers are expected to have high electron conductivity and high mass transport [49]. This fact can help explaining the differences in cell activity. Although the current collectors are the same in both cases, water electrolysis can occur over electrode area that is not in direct contact with the current collector and still contribute for hydrogen production. Flow of electrons is driven by differences of potential on both sides and protons can be conducted through Nafion ionomer present in the catalyst layer, driven by concentration differential that exists between the two electrodes.

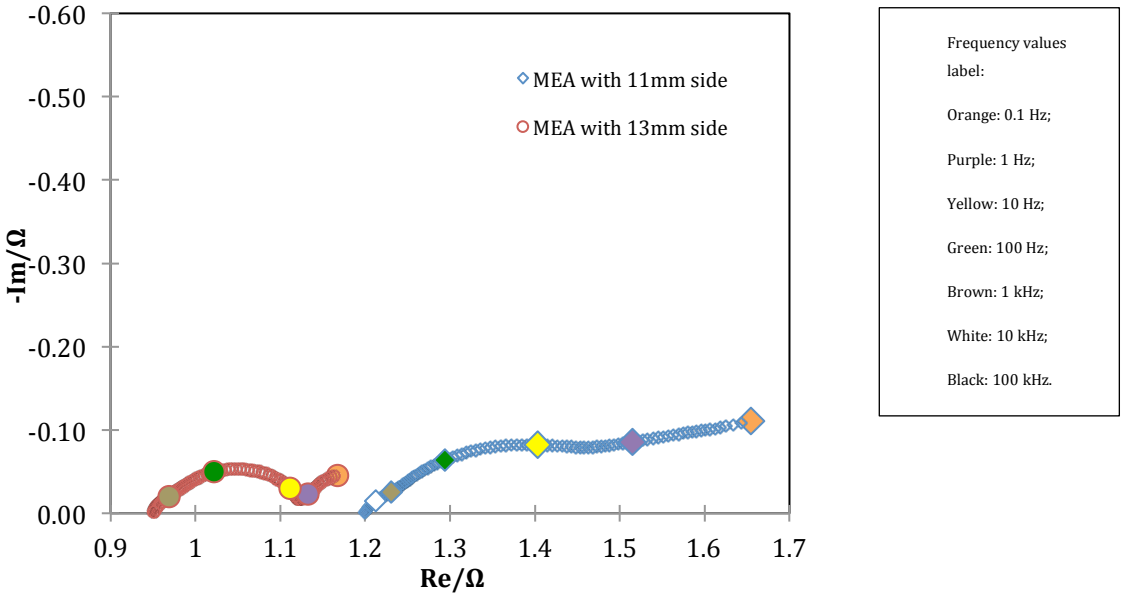


Figure 10 - EIS curves illustrating influence of MEA (from Solvicore®) size in cell impedance. Performed @ 2 V and 22 °C.

EIS data in Figure 10 show impedance measurements to the cell with both MEA sizes. Impedance signals, of the two measurements, do not start at the same value of real impedance. This translation

suggests that overall ohmic resistance differs between both cell assemblies [50]. Possibly, larger areas between MEA and current collector sizes help to get a more uniformly distributed pressure in the cell assembly and consequently less contact resistances.

It can also be seen that between medium and low frequencies range, it is much more difficult to trace arches with the smaller MEA than with the larger MEA. This indicates a contribution of more than one type of resistance. Still, it is possible to recognize that the absolute value of real impedance of the cell with the smaller MEA is bigger. This is in accordance with the lower performance shown in the potentiostatic polarization of both assemblies.

4.1.2 – Electrochemical activity influence of gasket use in cell assembly

Trying to accomplish a high reproducible assembly, one frame shape of Ice Cube Sealing 35 FC-PO 100 gasket was used. The goal was to center the MEA with current collectors in the middle of the bipolar plate, in order to have a good pressure distribution when a clamp held the cell. This study was, again, performed with the experimental MEA from SolviCore with 11 mm of square side size.

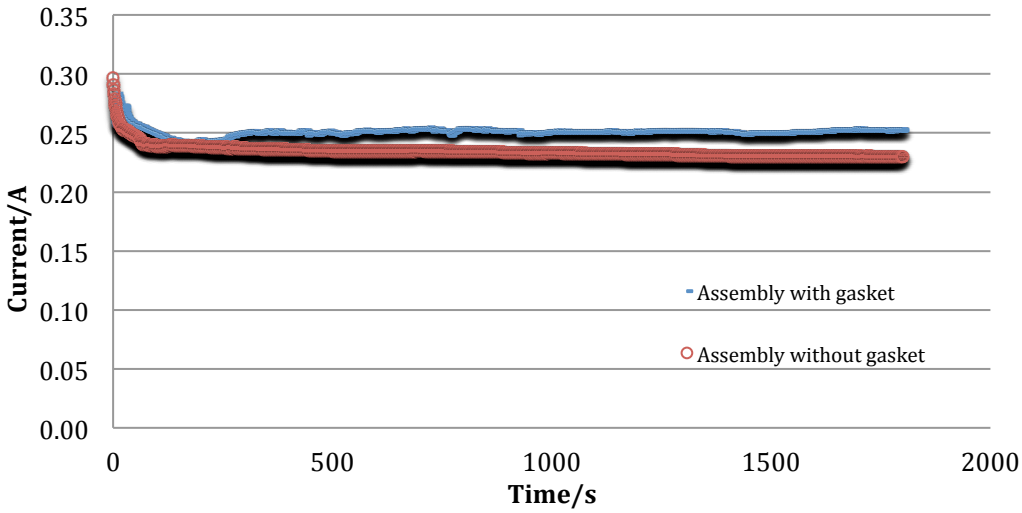


Figure 11 - PEM electrolyzer potentiostatic polarization curves of assemblies with and without gasket @ 2 V and 22 °C (MEA from Solvicore®).

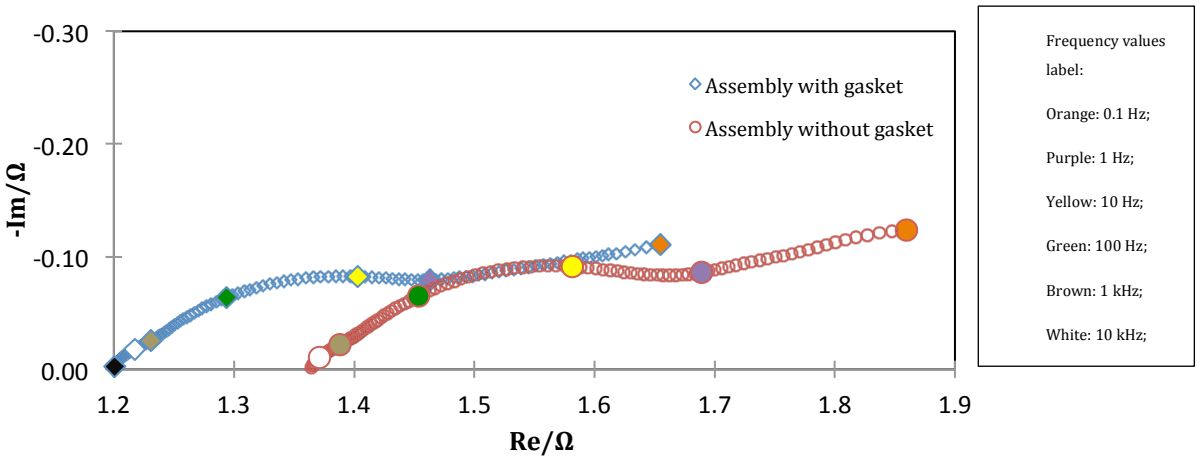


Figure 12 - PEM electrolyzer EIS curves of assemblies with and without gasket @ 2 V and 22 °C (MEA from Solvicore®).

From the polarization curves of the two assemblies (Figure 11), it is possible to identify a small difference of performance. With help from EIS measurements of both assemblies (Figure 12), it is possible to identify a general cause for performance difference. Impedance measurements of both assemblies have similar shape and approximate value of total impedance. But there is a translation of the two curves along the real impedance axis. As it was stated in the previous study, this translation is related with ohmic resistances [50]. The explanation for this ohmic resistance might have its origin in the first reason that lead to this study: help centering the MEA and current collectors in the center of the bipolar plate providing lower ohmic resistances.

4.1.3 – Electrochemical activity influence of membrane pre-treatment

The pre-treatment consists in membrane protonation improvement, boiling them in mineral acids. Ultimate branch of commercialized Nafion® membranes is claimed to be chemically stable and protected with protection foils. It was assumed that membranes would be ready to coat right after removing the protection foils. Three MEAs were electrochemically tested to assess the effect of boiling in mineral acids. Boiling in a mineral acid would improve the protonic form of the membrane [48]. The chosen mineral acids for boiling the membranes were sulfuric and nitric acids, diprotic and monoprotic acids, respectively.

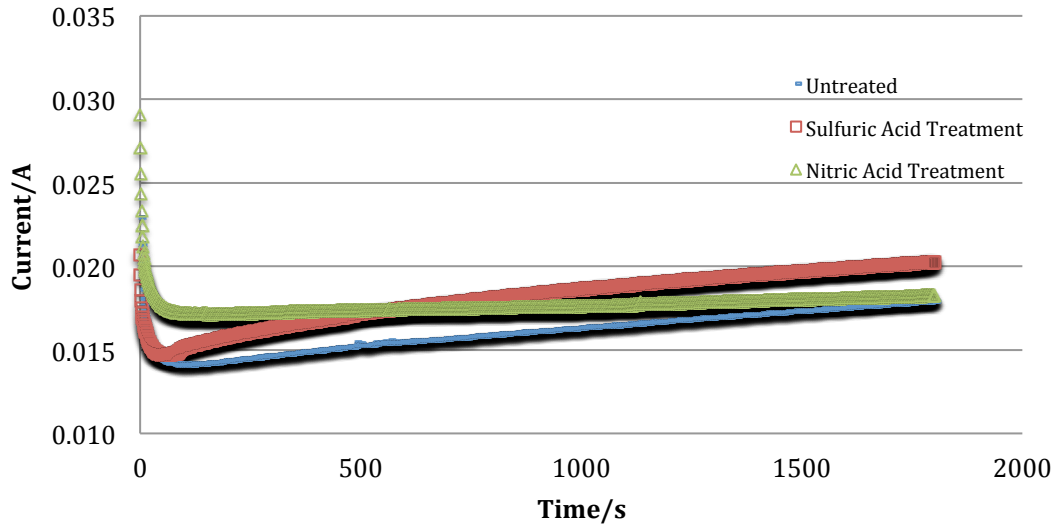


Figure 13 - PEM electrolyzer potentiostatic polarization curves of MEAs with and without pre-treatment to the membrane @ 2 V and 22 °C - pre-treatment study. MEAs coated with Ir mixture in the anode and Pt/C in the cathode by screen printing method.

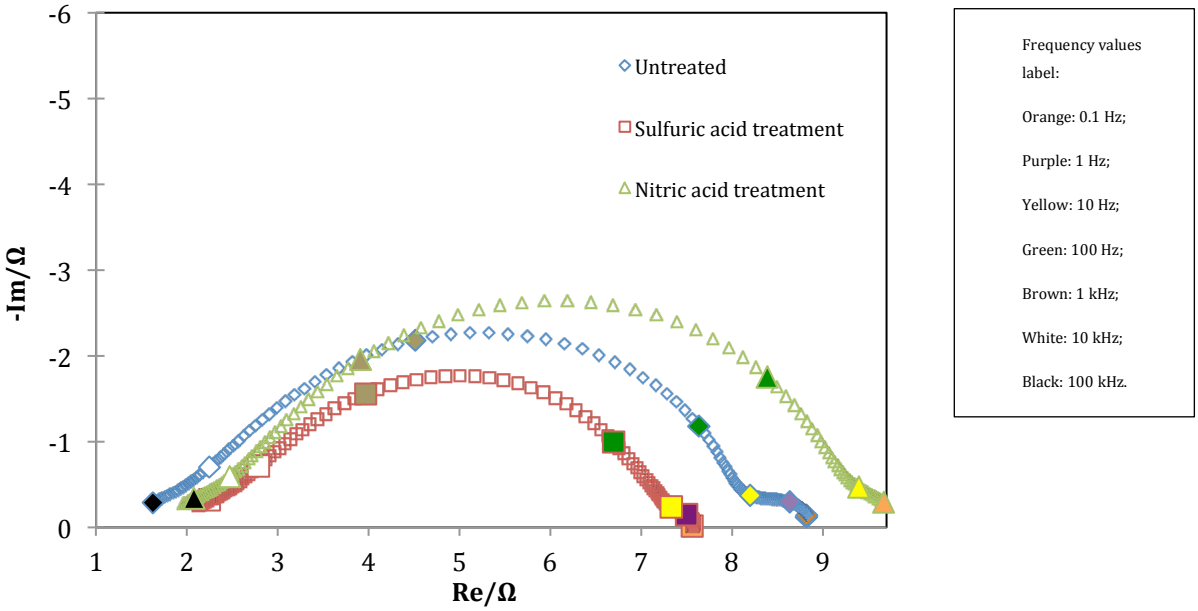


Figure 14 - PEM electrolyzer EIS curves of MEAs with and without pre-treatment to the membrane @ 2 V and 22 °C - pre-treatment study. MEAs coated with Ir in the anode and Pt/C in the cathode by screen printing method.

From the three polarizations curves in Figure 13, the first fact that stands out is the improvement of performance of the three MEAs along time. The membrane boiled in H_2SO_4 shows better transient activity, for longer values of time, than the one boiled in HNO_3. This could have to do with extra protons that sulfuric acid (diprotic) can provide in relation to nitric acid (monoprotic).

Between the untreated and pre-treated MEAs, activity differences are larger in the beginning, but this is decreased with the running time of the cell. This fact suggests that pre-treated MEAs show a fugacious better activity, when compared to the untreated membrane. It is possible to exist some acid traces in the water feeding coming from the MEAs. If this is true, the electrolyzer shows better activity because the water bath can become co-acting as proton conductor (H_3O^+) between the anode and the cathode for short values of time.

EIS measurements in Figure 14 were performed after polarization curves in Figure 13. Although the membrane pre-treated with sulfuric acid still showed better electrochemical behavior, this treatment was not considered as critical for MEA fabrication for two main reasons: longer processing time with small and temporary improvement in activity; boiling procedure can physically damage the MEAs.

4.1.4 – Study of MEA electrochemical activity growth

It was mentioned in the previous study that an unexpected growth of the current could be seen. This fact awoke a lot of curiosity and interest, because it would be expected that current values would stay constant after some time, as it happens with tested commercial MEAs. A decrease in cell activity would be much more common, suggesting degradation issues. Although this performance improvement was found to be weird, it was tried to reach the highest possible activity with the developed MEA. Companies that produce MEAs for PEM electrolysis do not mention if they perform some kind of activation to their MEAs before commercializing them.

The MEA that was used was the MEA without pre-treatment from the previous study. It was submitted to a potentiostatic polarization over 2.5 hours (Figure 15) in order to try to reach a constant value for the current. Before and after the mentioned potentiostatic polarization, 30 minutes of potentiostatic polarizations were also recorded (Figure 16). This sequence was made, not only to try to reach the maximum current of the cell but also to assess if, after disassembling and assembling the electrolyzer cell, electrochemical activity improvement would be verified and consistent.

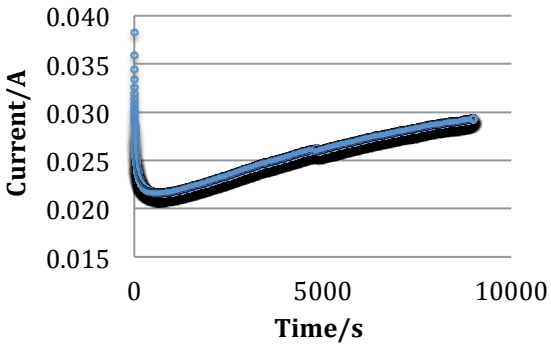


Figure 15 - PEM electrolyzer 2.5 hours potentiostatic polarization curve of MEA coated with alpha - terpineol as solvent in Ir based paste @ 2 V and 22 °C. MEA coated with Ir in the anode and Pt/C in the cathode by screen printing method.

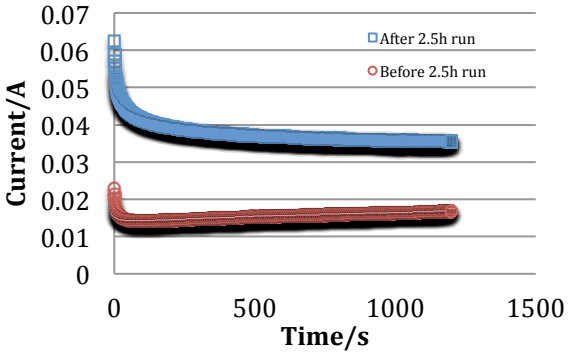


Figure 16 -PEM electrolyzer 30 minutes potentiostatic polarization curves of MEAs before and after a 2.5 hours run @ 2 V and 22 °C - activity starting point study. MEA coated with Ir in the anode and Pt/C in the cathode by screen printing method.

In Figure 16 it is possible to notice that the performance improvement during 2.5 hours of polarization was effective. Although the two records show transient activity behaviors, the gap between the two curves is considerable and approximately equivalent to the electrochemical activity growth seen in Figure 15. These short time polarizations (30 minutes) were performed with a new assembly of the cell.

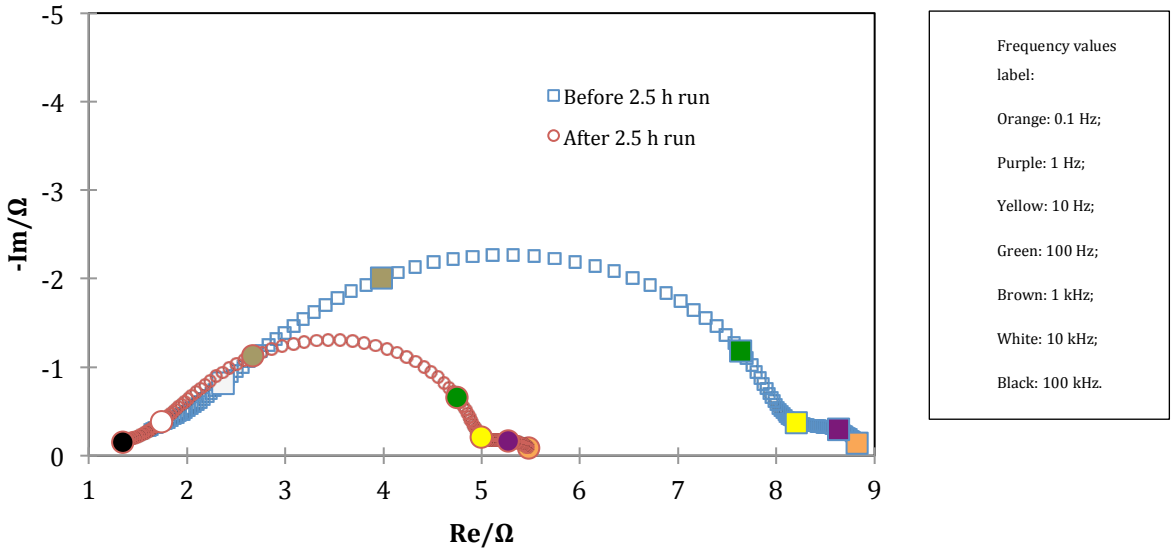


Figure 17 – PEM electrolyzer EIS curves of MEAs before and after a 2.5 hours run @ 2 V and 22 °C.

EIS curves in Figure 17 were recorded immediately after polarizations of Figure 16. They show a considerable reduction of the total resistances of the MEA. The shape of the two curves is similar,

which leads to the thinking that the same type of resistances might be present. However, differences between the two curves can be thanks to one or more contributions. OER related losses contribute with the biggest part of an electrolyzer impedance spectrum (eight times bigger than the losses contribution from HER) [46]. In Figure 17, it is possible to notice that most of the total impedance of each curve comes from the biggest single arch. Having both curves with the same shape, it might be possible to get approximately each curve from the other by only changing the biggest single arch. This argument leads to the fact that the biggest contribution, on cell performance improvement, comes from electrochemical mechanisms related with the anode side of the MEA.

The absolute origins that cause this improvement in the anode activation overpotential are difficult to identify without a more intensive and directed study. But some hypothesis can be considered. Besides the prepared MEA was considered completely coated and dried, some alcohol smell could be felt. This might suggest that some remaining organic solvent was still on the catalyst layers, although a more effective drying procedure to remove any smell was not possible to reach without damaging the membranes. The strong oxidizing environment existing in the anode side of the cell (potential is 2 V) could be oxidizing the remaining solvent, while the cell is running. The influence of any remaining solvent with the microstructure of the catalyst layer is not well known. It is possible that a continuous oxidation of the solvent can allow more adsorption of water in the catalyst surface, not only by improvement of catalyst layer porosity but also diminishing physical competition (it is known that water can easily bond with alcohols through hydrogen bridges). A more extensive potentiostatic polarization during 15 hours (Figure 18) was performed with the objective of reaching a stationary activity behavior of the developed MEA.

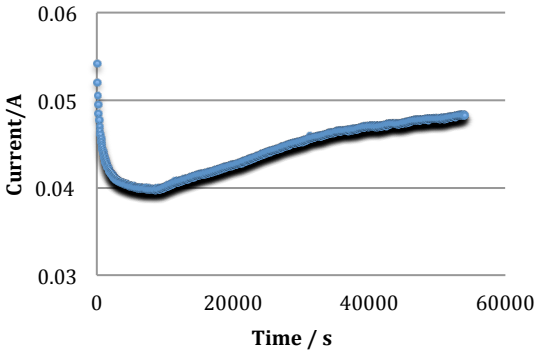


Figure 18 - PEM electrolyzer potentiostatic polarization curve of MEA coated with alpha - terpineol as solvent in Ir based paste @ 2 V and 22 °C. MEA coated with Ir in the anode and Pt/C in the cathode by screen printing method.

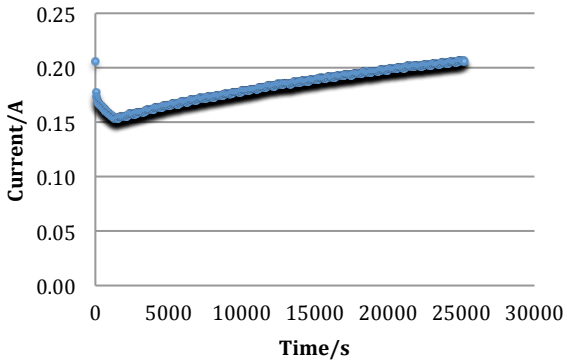


Figure 19 - PEM electrolyzer potentiostatic polarization curve of MEA coated with alpha - terpineol as solvent in Ir based paste @ 2 V and 40 °C. MEA coated with Ir in the anode and Pt/C in the cathode by screen printing method.

The fact that a stationary current value was not reached with 15 hours of polarization - Figure 18; lead to another long polarization (9 hours), but with a temperature control system on the water. The intention of running the cell at 40 °C was to accelerate activity improvement. After the polarization that is plotted in Figure 19, a constant value for the current was still not reached. Electrochemical measurements to this MEA were stopped at this point. Although the maximum activity of an MEA can only be measured when the polarization shows a stationary behavior, this was not performed thanks to some timing planning limitations.

In order to compare the final stage of improvement of electrochemical activity of the developed MEA with the experimental MEA from Solvicore®, it was performed a potentiostatic polarization under the same operating conditions as used in polarization of Figure 19.

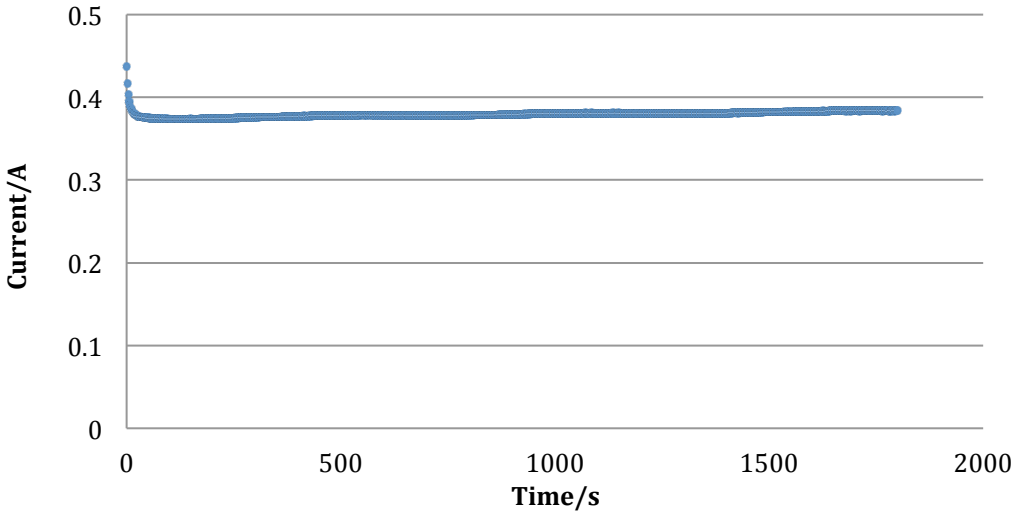


Figure 20 - PEM electrolyzer potentiostatic polarization curve of an experimental MEA from Solvicore® @ 2 V and 40 °C. Commercial MEA with Ir and Pt in the anode and cathode respectively.

Obtained a constant value of the MEA from Solvicore® of approximately 0.38 A at 2 V, it is possible to compare the two MEAs. At the last stage of the developed MEA, without any pre-treatment, approximately 55% of the performance of the experimental MEA from Solvicore® was reached. It should be emphasized that this value certainly would be higher (not knowing when or for how long) if the developed MEA was put to run until reaching the stationary behavior.

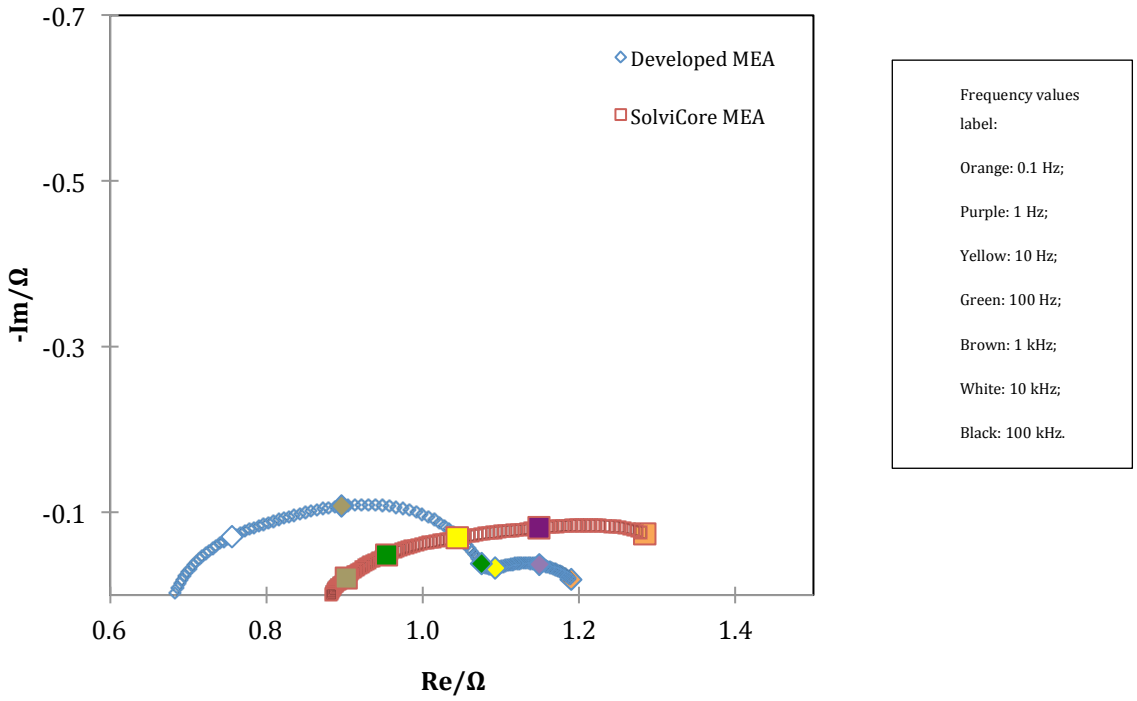


Figure 21 - PEM electrolyzer EIS curves of MEA coated with alpha - terpineol as solvent in Ir based paste and an experimental MEA from Solvicore® @ 2 V and 40 °C.

Comparing the EIS measurements from Figure 21 it is possible to identify that the curves cross the real impedance axis at different values. Again, this is due to different ohmic resistances [50]. Cleaning between different assemblies fought formation of an oxide layer, but some resistance effects could have occurred. Although it is difficult to identify and compare which type of resistances in both MEAs have more contribution to the absolute resistance value. The developed MEA shows an inflexion point, that cannot be seen in the MEA from Solvicore®, indicating the existence of more types of resistances.

4.2 – Second part of electrochemical tests results

As referred before, the second part of electrochemical results differs from the first part in the electrocatalyst used in the anode, cell size assembly and operation conditions. The last difference, that was not mentioned yet, was the coating method of the cathode. Wet spraying method was used to coat the cathode of the following MEAs with a suspension using Pt/C (60% by mass) as supported catalyst. The intention was to focus on the development of the anode electrocatalyst layer, coating the cathode with an already well-known process at DLR. The anode was screen

printed with ink containing Iridium Black as catalyst and Ti_4O_7 as support. The catalyst loadings were 0.4 mg cm^{-2} of Ir in the anode and 0.5 mg cm^{-2} of Pt in the cathode.

In this second part, a commercial MEA (e300) from Solvicore was used as performance reference for the developed MEAs. All the potentiostatic polarizations of this part were performed at 1.7 V. The operation temperature was set at 40 °C. EIS measurements were done in galvanostatic mode at 0.14 A. This change in the impedance measurements has to do with the conventional form of performing electrochemical tests to electrolyzers. Establishing a current value and measure the cell potential is the convention, because the main goal in electrolysis is to produce hydrogen and its produced quantity is directly related with the power density.

Along the project, the aim was to produce a good coating for the anode side of the MEA. This is related to the fact that anode mechanisms are dominant in terms of MEA resistances. Thereby the cathode side was coated with a well-known protocol in DLR (wet spraying method of a Pt/C suspension). This decision was influenced by the suspicion, from the first part of electrochemical tests, that any remaining solvent (α - terpineol) in the catalyst layer of the cathode could not be oxidized (thanks to low potential values at the cathode).

4.2.1 – The role of organic solvents preparing the anode side of the MEA

Coating recipes for electrodes of any PEM cell depend on the coating method. Following the literature references and trying to keep the coating system as simple as possible, it was lead to define that the only material that could change the coating system would be the organic solvent. Ratios between the coating materials were kept constant in order to evaluate the single effect of the solvent properties in the overall electrochemical behavior the electrolyzer.

Three coating systems were studied, changing the organic solvent of the catalyst pastes. Ethane-1,2-diol; propan-1,2-diol and cyclohexanol were the chosen organic solvent for the three pastes. This choice was taken considering literature research and some basic principles and assumptions from solvents' physical properties. The prepared pastes in this solvent study were prepared mixing and milling the paste with a mortar and a pestle. The membranes were coated in a square area of 16 cm^2.

Before compare any solvent effects it was needed to get a good coating reproducibility. To accomplish that reproducibility, two MEAs of each system were supposed to be prepared and electrochemically tested hoping to get similar electrochemical behavior. The first paste to be coated was prepared with ethane-1,2-diol as a solvent. Electrochemical data (potentiostatic polarization and EIS curves), and a photo of the coated anode in shown below.

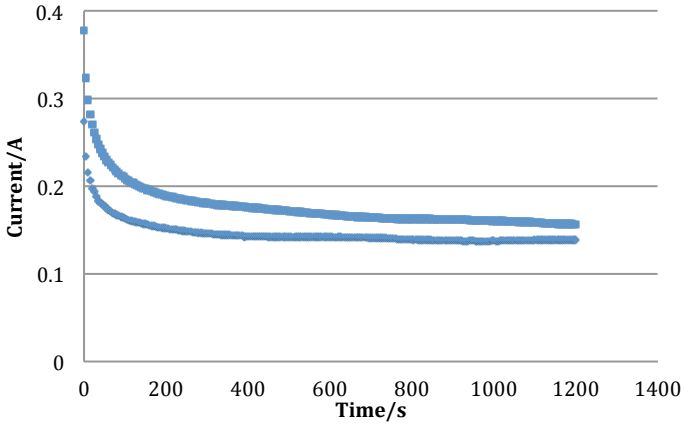


Figure 22 - PEM electrolyzer potentiostatic polarization curves with MEAs coated with ethane-1,2-diol as solvent in Ir with Ti_4O_7 paste @ 1.7 V and 40 °C - reproducibility assessment.

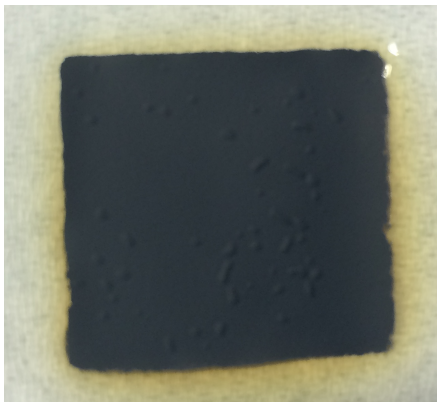


Figure 23 - MEA anode coated with ethane-1,2-diol paste.

The initial intention of showing electrochemical results was to perform potentiostatic polarizations to the MEAs during 3 hours. A technical problem caused the loss of that curve for one of the MEAs prepared with ethane-1,2-diol as a solvent. To overcome this obstacle, after both MEAs were submitted to the initially desired polarization during 3 hours, they were submitted to a second polarization for 30 minutes (Figure 22).

It is possible to assess from Figure 22 that both MEAs reveal a close electrochemical behavior, attesting an acceptable reproducibility of this coating system and procedure. However, Figure 23 shows that this coating cause swelling to the membrane. It is well known that swelling of the membrane is critical in PEM fuel cells [3]; but its electrochemical effect on PEM electrolyzers is still not well known. Although the swelling is masked after hot pressing the MEA, certainly it is a severe obstacle to achieve a good coating reproducibility.

The next coating system to be studied was a paste prepared with propan-1,2-diol as a solvent. Figure 24 shows the collected electrochemical data. Three hours lasting polarizations are shown for this system.

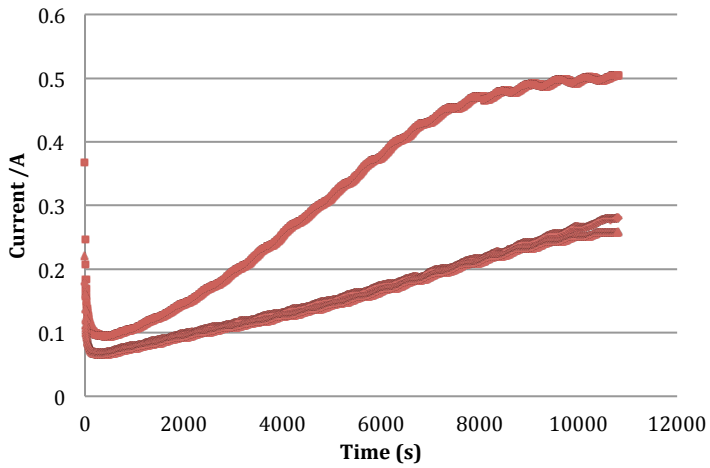


Figure 24 - PEM electrolyzer potentiostatic polarization curves with MEAs coated with propane-1,2-diol as solvent in Ir with Ti_4O_7 paste @ 1.7 V and 40 °C - reproducibility assessment.

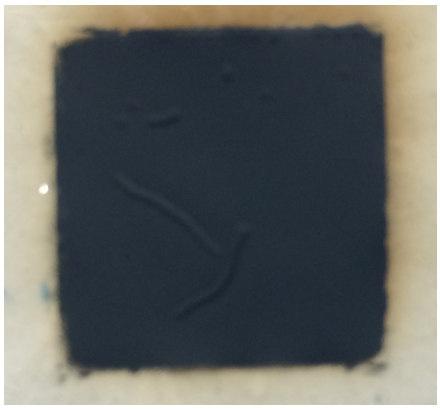


Figure 25 - MEA anode coated with propan-1,2-diol paste.

Thanks to large differences in performance during polarization time of one of the curves, there was the need to test a third MEA with this system. The third curve attested the reproducibility of this coating system. Membrane swelling can be noticed in Figure 25. This swelling pattern is different from the one from Figure 23. This membrane swelling is larger, less frequent and less homogeneous.

Some hypothesis for this electrochemical difference can be related to irregular homogeneity of the prepared paste. Poor mixing of the catalyst with the support, particles size and irregular solid content of the paste could cause surprising effects on MEA activity. Although the calculated catalyst loading is the same, none of these three aspects influence could be objectively quantified in the planned working time of this project.

The last coating system to be studied was the paste prepared with cyclohexanol as solvent. Three MEAs were tested to assess a better reproducibility judgment after the problem that happened with the last coating system.

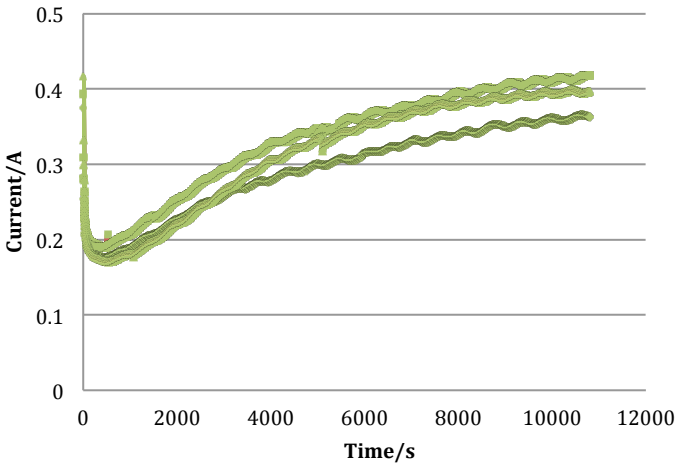


Figure 26 - PEM electrolyzer potentiostatic polarization curves with MEAs coated with cyclohexanol as solvent in Ir with Ti_4O_7 paste @ 1.7 V and 40 °C - reproducibility assessment.

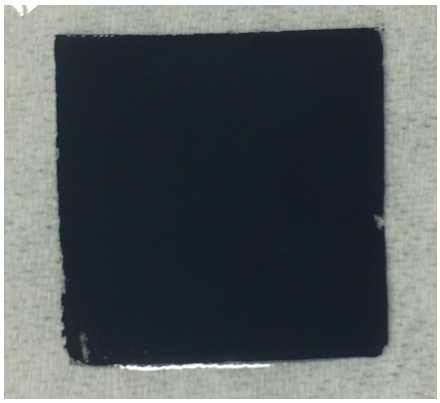


Figure 27 - MEA anode coated with cyclohexanol paste.

The three curves in Figure 26 show an acceptable reproducibility if it is taken into account the discrepancy of the system with propan-1,2-diol as solvent, and the difficulty on maintaining paste properties with a solvent that needs to be heated in order to be processed. But the best achievement of this system is not to cause any swelling to the membrane (Figure 27). The coating surface looked homogeneous and flat. The thickness of the dried coated layer is 13 µm.

After achieving an acceptable reproducibility of the prepared MEAs, it is important to compare the effect of the three solvents on cell electrochemical performance. It was chosen to plot the best and reproducible MEA from each coating system.

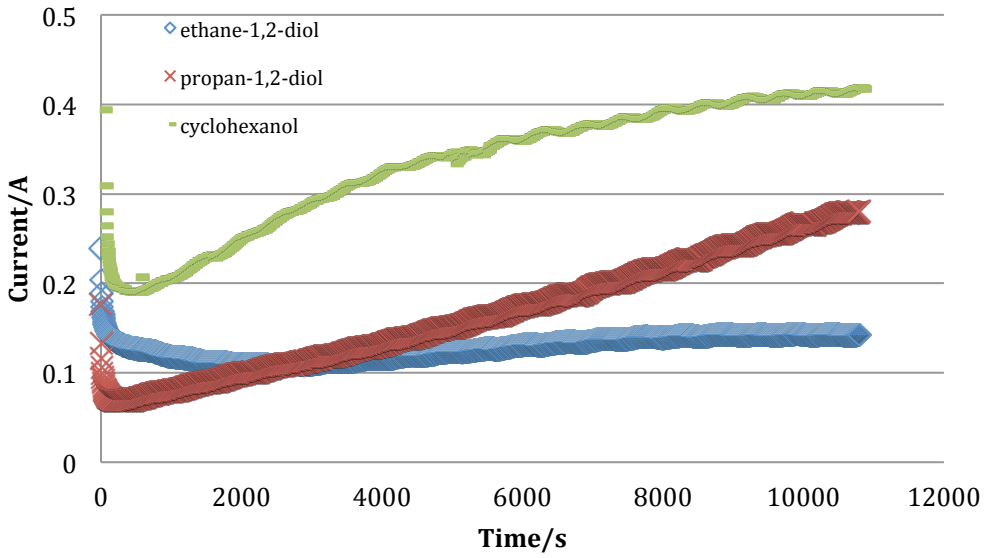


Figure 28 - PEM electrolyzer potentiostatic polarization curves with three MEAs coated with three different solvents in Ir with Ti_4O_7 paste @ 1.7 V and 40 °C - reproducibility assessment.

From Figure 28, differences of electrochemical activity (in transient behavior) are very different. Although a constant value for the current should be reached, issues related with project time this was not possible. The system with ethane-1,2-diol has the lowest electrochemical activity and only shows a small improvement in MEA activity. The slope of the propan-1,2-diol curve is slightly larger than the slope of the cyclohexanol curve. The choice for the best system should not only be based on electrochemical activity but also on reproducibility of the processing. Although some care is needed while preparing and coating with the paste with cyclohexanol as solvent, the fact that this system does not cause any swelling to the membrane was considered a big breakthrough.

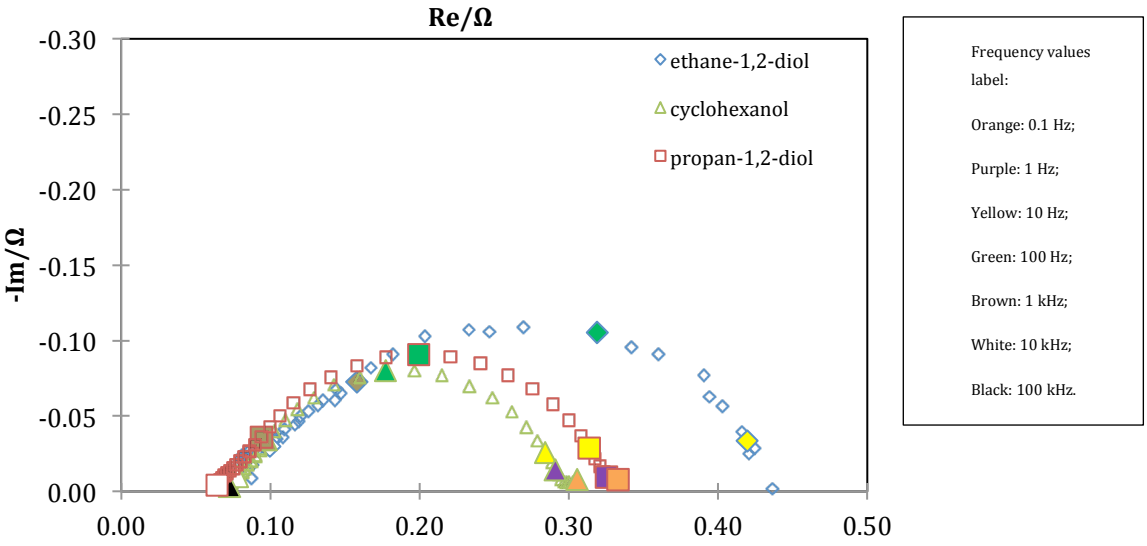


Figure 29 - PEM electrolyzer EIS curves with three MEAs coated with three different solvents in Ir with Ti_4O_7 paste @ 140 mA and 40 °C - reproducibility assessment.

Impedance measurements, shown in Figure 29, demonstrate that the cell with the MEA anode coated with cyclohexanol based paste is the one that has lowest absolute resistance, followed by propan-1,2-diol based paste. It can also be seen that ohmic resistances between the three assemblies are equivalent [50].

The choice of studying these three solvents for the anode coating paste was essentially based in their physical properties (Table 3). The physical properties of α -terpineol are also shown, in order to compare all the used solvents in screen-printing pastes.

Table 3 - Physical properties of organic solvents used in screen printing pastes.

Solvent	Viscosity (Pa s) @25 °C	Vapor pressure (mmHg) @ 20 °C	Dielectric constant/ε	Boiling temperature (°C @ 760 mmHg)
α - terpineol	0.03650	10.5	2.8 @22 °C	219.0
ethane-1,2-diol	0.01613	0.06	37 @ 25 °C	197.6
propan-1,2-diol	0.04200	0.13	32 @ 20 °C	188.2
cyclohexanol	0.05460	1	15 @ 20 °C	161.0

Taking a closer look to the properties values range, mentioned in [3]; for a suitable organic solvent for screen printing pastes:

- all the four solvents respect the interval of viscosity (0.016 Pa s $< \mu < 0.060$ Pa s);
- evaluating their values of vapor pressure, α – terpineol would have the slowest evaporation rate followed by cyclohexanol.
- regarding the dielectric constant, α – terpineol would be the only solvent that would make Nafion ionomer precipitate ($\varepsilon < 3$) while the other three solvents would make Nafion ionomer stay in solution form ($\varepsilon > 10$).

The most probable causes for different electrochemical performances of the tested MEAs might have to do with swelling issues and the dielectric constant values of the solvents. In fact both mentioned hypothesis might be connected to each other. The way that organic solvents interact with Nafion® molecular structure may cause some differences in the catalyst layer microstructure.

Relating the values of the dielectric constant of each solvent with the activities obtained with the three coating systems, it is easy to notice that the solvent with the lowest value of dielectric constant belongs to the coating system with better electrochemical activity. The solvent, with highest value of dielectric constant, is part of the coating system with lowest electrochemical activity. In [41]; the authors related the dielectric constant of organic solvents used in catalyst inks with triple phase boundary conditions. They only categorized triple phase conditions within certain boundaries of dielectric constant values. They claim that triple phase boundary conditions are improved when $\varepsilon > 10$, without telling anything about if the distance from that boundary point would be better or worse for the anode layer microstructure in terms of overall performance.

In [42] the authors stated that Nafion ionomer in "colloidal" form would offer the best triple phase conditions. Some authors already denied this statement [51,52]. Still, it is possible that keeping Nafion ionomer in solution form, but close to the "colloidal" form border ($\varepsilon \geq 10$), can bring an improvement of triple phase boundary conditions. "Colloidal" form of the ionomer makes it more prone to be deposited on the catalyst particles surface. This can increase the amount of active sites

in the catalyst layer, but the overall performance will only be improved if there is a complete path for protons to diffuse from the catalyst surface to the electrolyte. Additionally, authors from [27] tell that supported catalysts, usually, are well dispersed and extend deep into layers with support particles, requiring more ionomer to extend the triple phase boundary. Besides Ti_4O_7 is used as support of iridium black, the two powders were only mixed together during paste preparation. Then, ionomer distribution (with solvents with high values of dielectric constant) is not as critical as it would be to more complex catalyst configurations. According to this reasoning, trying to gather advantages and still diminishing some disadvantages from both forms can be interesting to accomplish. For this, some more complicated coating systems could be developed (using a mixture of two or more organic solvents in order to reach some specific physical properties in the catalyst paste).

It is very interesting and promising the fact that pastes with cyclohexanol as a solvent did not swell the membranes during coating. This breakthrough was also achieved with pastes with α - terpineol as a solvent. But membrane swelling occurred when ethane-1,2-diol and propan-1,2-diol were used in screen printed pastes. In general, the uptake of polar solvents, from the membrane, exceeds that of non-polar for the pure solvent case [34]. Taking a superficial look to the molecular structure of the four solvents, there are two main differences. Cyclohexanol and α - terpineol have a cyclic structure and only one hydroxyl group. On the other hand, ethane-1,2-diol and propan-1,2-diol have linear structure and two hydroxyl groups. The cyclic structure has more influence in decreasing the effect of the polarity provided by the hydroxyl group than the one provided by a linear structure. Additionally, two hydroxyl groups in the same molecule provide more hydrogen bridge bonds with the sulfonated groups than if the molecule has only one hydroxyl group. These molecular features could explain the membrane swelling behavior among the four solvents.

It is in the interest of this project to compare electrochemical results with commercial MEAs, even though some important parameters are different. A potentiostatic polarization to e300 MEA from Solvicore® is plotted in Figure 30 and EIS measurement was also performed and compared to the developed MEA with cyclohexanol as solvent of the coating paste.

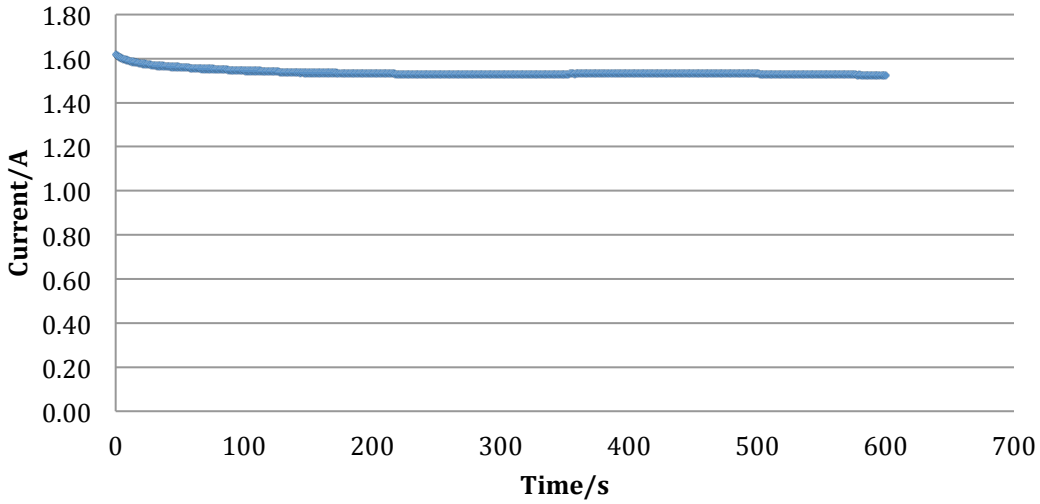


Figure 30 - PEM electrolyzer potentiostatic polarization curve commercial MEA e300 from Solvicore® @ 1.7 V and 40 °C.

The developed MEA, at its last stage of electrochemical activity improvement, showed approximately 30 % of the electrochemical activity of e300 MEA. Although this value might not seem so satisfactory, it should be considered that the anode catalyst loading of the developed MEA is 0.4 mg cm^{-2} and most of commercial MEAs have around five times more catalyst loadings in the anode.

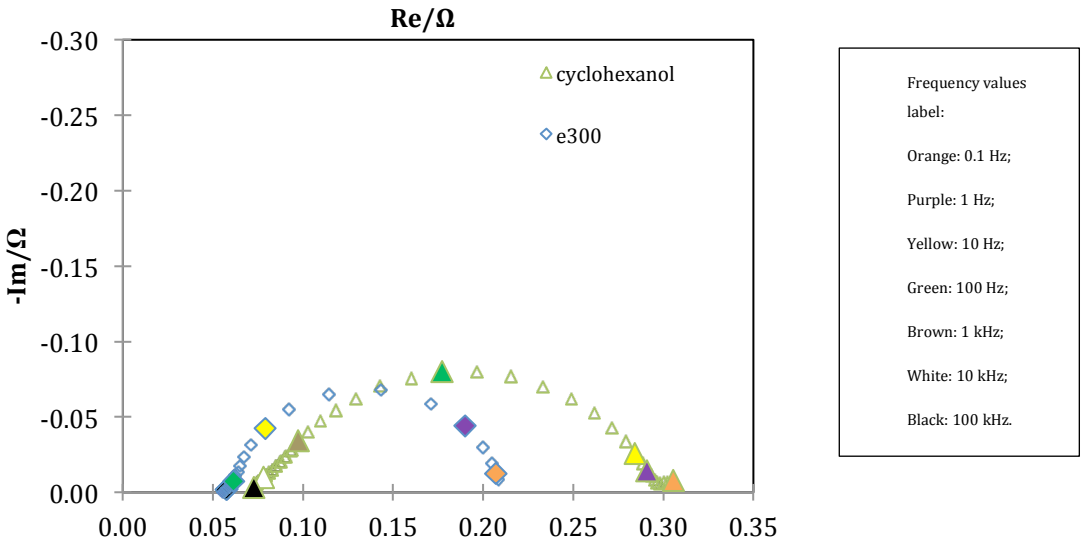


Figure 31 – PEM electrolyzer EIS curves of a commercial MEA e300 from Solvicore® and the MEA prepared with cyclohexanol as solvent of the Ir and Ti_4O_7 paste @ 140 mA and 40 °C.

4.2.2 – MEA swelling treatment electrochemical effects

In the case of choosing an organic solvent for catalyst pastes that causes membrane swelling, it was performed a treatment to the membrane in order to minimize its swelling. The used MEAs were coated exactly in the same way as they were in the previous study, and the paste that was used for the anode coating had ethane-1,2-diol as solvent and 20 % of solid content in the paste. Before this experiment it was unknown if ionic reconversion to Na^+ form would limit swelling of the membrane, and more important if membrane conductivity would be compromised after the complete treatment.

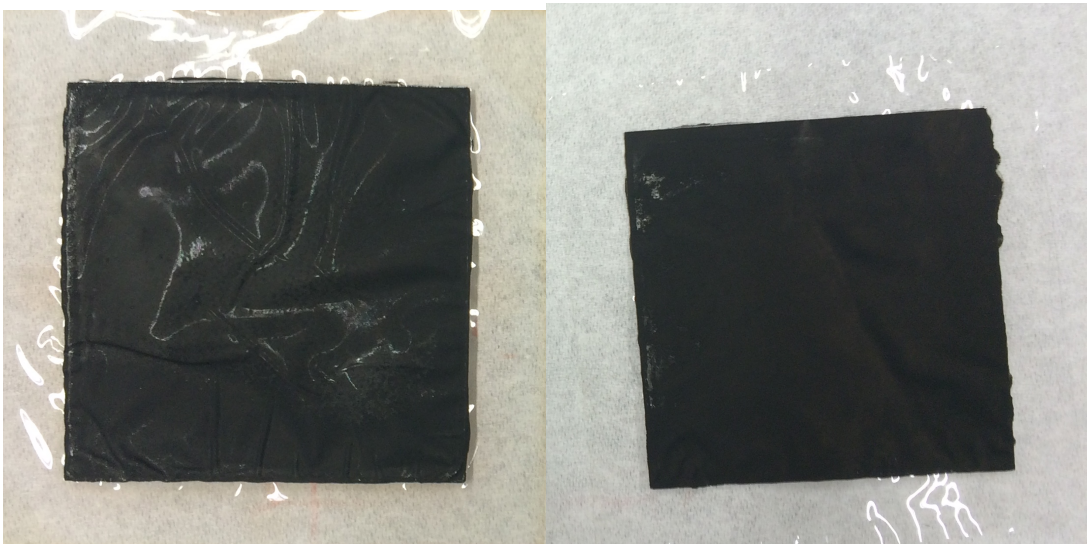
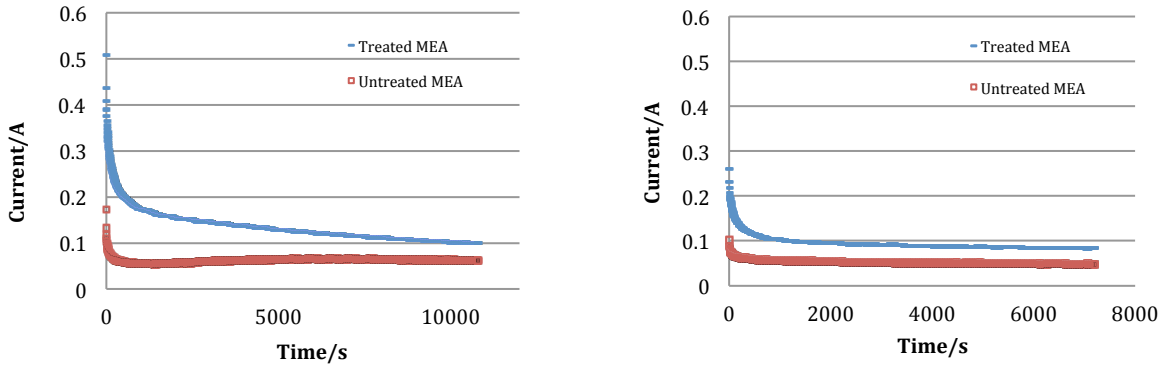


Figure 32 - MEA coated anodes without and with swelling treatement, respectively

In figure 32 the effectiveness of the swelling treatment is clear. Although, macroscopically, this treatment is effective, it should be found a way to boil the membranes (either before or after coating) without subjecting them to a so physically harsh environment. During reprotonation, the coated anode layer showed superficial scratches and possibly had some small losses of catalyst. The aim of these electrochemical measurements was to verify if a MEA subjected to swelling treatment would electrochemically perform as a MEA that was not subjected to this treatment.



Figures 33 and 34 - PEM electrolyzer potentiostatic polarization curves with MEAs coated with and without swelling treatment @ 1.7 V and 40 °C

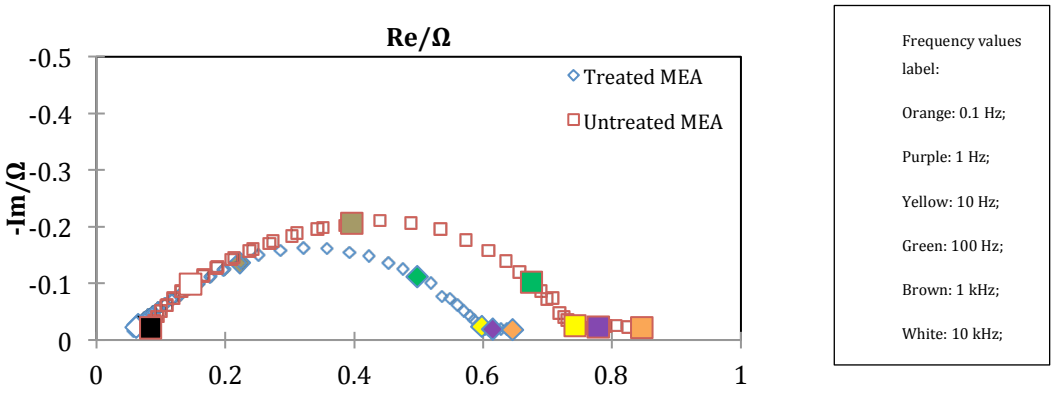


Figure 35- PEM electrolyzer EIS curves with MEAs coated with and without swelling treatment @ 140 mA and 40 °C

Data shown in Figure 34 was recorded immediately after data recorded in Figure 33. It is possible to notice that the difference of current values of both potentiostatic polarization curves is decreasing along time. The same explanation, as the one that was given in the study about membranes pre-treatments, could explain why the swelling treated MEA shows more activity in early times. Some remaining acid traces, left during reprotonation step, could mask the true cell electrochemical behavior. When those effects of the remaining H_2SO_4 disappear, a drop in activity occurs. In this study, the transient behavior of the curves is not the usual as it is in all prepared MEAs. A small but continuous drop in performance is noticeable for both MEAs in figure 34. This might have its origin in the catalyst layer. Degradation of the catalyst and/or support can be one possible cause.

5 - Conclusions

A MEA for PEM electrolysis prepared by coating electrocatalyst layers directly on the Nafion® membrane by screen printing was developed and characterized. It was reached 30 % of the electrochemical activity of a commercial MEA from Solvicore®. The developed MEA had 0.4 mg cm^{-2} of Ir in the anode and 0.5 mg cm^{-2} of Pt in the cathode, lower catalyst loadings when compared to the ones reported in the literature and with the values of commercial MEAs.

Pre-treatment of Nafion® membrane with mineral acids had a negligible effect on MEA activity. This fact allows decreasing in the processing time and avoids any possible damage of the membranes during boiling procedure.

Cyclohexanol proved to be the most suitable single solvent for the electrode pastes coated by screen printing directly on the membrane. Apart from providing the highest activity, it did not cause noticeable swelling to the membrane. The coated MEA with α - terpineol based paste showed 55% of electrochemical activity of an experimental MEA from Solvicore® (both had similar catalysts and catalyst loadings).

The performed swelling treatment was found effective for minimizing the membrane swelling during the coating process of the electrode pastes using ethane-1,2-diol as solvent. No decrease in electrochemical activity was found when compared with the same MEA without swelling treatment.

Reproducibility of the coating process was acceptable, but still there is room for improvements mainly during paste preparation stage (taking advantage of the use of the 3-roll mill machine). The speed of the coating process is high and comparable with industrial production times.

5.1 - Accomplished objectives

Among the objectives defined in the beginning of the project (high performance, high reproducibility and low processing time of the developed MEAs), they were relatively achieved. Regarding the last two objectives, they are directly related with the coating process. The process was clear and well defined therefore it is expected to be easy to replicate the results presented in this work. In terms of performance of the developed MEAs, more study about the electrochemical durability of the catalyst layers should be done. Besides the obtained electrochemical activity is relevant when compared with commercial MEAs, longer polarizations should be done in order to show the overpotential behavior along time and assess electrochemical degradation of developed MEAs.

It was also expected to get thin electrode layers and low catalyst loadings. As mentioned already in the discussion, each produced layer had 13 μm of thickness (the used membrane has 51 μm). Electrocatalyst layers were coated with approximately five times less catalyst loadings of commercial MEAs. This outcome is very important for PEM electrolysis in general, because some of the main drawbacks of the technology are the high price and availability of precious metal catalysts.

5.2 - Other performed works

During this six months work, some extra works were performed inside the scope of PEM technology. Although these works are not reported in this document, they represent promising and interesting topics for future research.

It was developed and electrochemically tested MEAs for PEM fuel cells. These MEAs were prepared by coating catalyst layers directly on the membrane and also on the gas diffusion layer. Although the electrochemical results were insignificant when compared to commercial MEAs, it is believed that a highly reproducible coating process could be achieved taking most of the considerations from the work developed for PEM electrolysis.

It was tried to take advantage from Nafion membranes leftovers by dissolving them in low weight organic solvents and produce a Nafion ionomer solution with controlled Nafion content. Complete dissolution was not reached, but it is believed that with some equipment that was not available during this project this could be overtaken (use methanol to help in the dissolution or dissolving Nafion particles with temperatures around 250 °C).

5.3 - Limitations and Future Work

There is room for improvements of the coating process and for its theoretical assumptions. Some possibilities for those improvements were identified and could be assessed with more time for research, because it is thought that equipment and materials availability from DLR was enough to make valuable research about the topic of this work.

A statistical study about catalyst loadings should be done in order to establish ideal weight measuring conditions of the membranes before and after coating. Thanks to the high adsorption of water by the membrane, it can cause considerable discrepancies in the weight measuring. These could be minimized if it was guaranteed the same relative humidity values before and after coating.

Recipes for pastes can be studied a bit further. There is any study in the literature about Nafion ionomer weight relation with catalyst particles in the scope of PEM electrolysis. More complex

solvent systems for screen printing pastes could be developed. A solvent system with a mixture of two or more organic solvents can be used to reach desired values of physical and chemical properties by playing with solvents ratios in the mixture.

One final catalyst paste was prepared using the 3-roll mill machine to mix Ir, Ti_4O_7, Nafion ionomer and cyclohexanol. It was expected to observe better MEA electrochemical performance when compared with the one coated with the paste mixed with the mortar and pestle. Although it was not verified (it was 4 times lower), some more study about the ideal gaps between the rolls considering the size of the catalyst and support particles. Gaps below sub-micrometers range can destroy the ceramic support particles compromising the electrochemical potential of the catalyst layer.

Longer potentiostatic polarizations should be performed, not only to achieve the maximum current values but also to study electrochemical degradation of the catalyst layers.

5.4 - Final assessment

The outcomes from these six months work cannot be confined to the achievements of some of the objectives mentioned in the project presentation. Through this work, I collected a wide insight about not only PEM electrolysis but also PEM fuel cells. Coating techniques principles were also a very relevant learned know-how. In general, the experience of doing research intercepting different technologies was very challenging and rewarding.

I believe that a deeper research about related topics mentioned in this thesis could be very valuable for DLR. PEM technology research groups could be able to produce their own MEAs. In the future, this could solve some problems related with the use of commercial MEAs in scientific research, like high cost and lack of technical information.

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